INORGANIC COLLOID
CHEMISTRY

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BY

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VOLUME II

THE HYDROUS OXIDES AND HYDROXIDES

PREFACE

Inorganic Colloid Chemistry is the general title of a three-volume treatise on the colloidal behavior of the elements and their inorganic compounds with special reference to the rôle they have played in the development of the modern theories and applications of colloid chemistry. The first volume, dealing with the elements in the colloidal state, was published two years ago. The present book, which is concerned with the colloidal properties and applications of the oxides, will be followed by one on the colloidal inorganic salts.

The title of this volume, The Hydrous Oxides and Hydroxides, suggests that it is a revision of the author's book, The Hydrous Oxides, written ten years ago and published by the McGraw-Hill Book Company. Actually, however, this volume represents more than a revision of the earlier work. During the past decade the numerous investigations of a large number of scientists in this country and abroad have greatly extended the knowledge of this important class of compounds and have modified appreciably certain of the older views concerning their colloidal behavior. Accordingly, most of the chapters in the older book have been entirely rewritten. In certain cases it was necessary to change even the chapter headings since recent applications of x-ray analysis methods have disclosed that many preparations believed to be hydrous oxides ten years ago are now known to be hydrous hydroxides or hydrous oxide hydrates.

The plan of this volume is as follows. After a chapter dealing in a general way with the preparation, properties, and nature of hydrous oxide sols and gels, separate chapters are devoted to the hydrous oxides of iron, the aluminum family, and chromium. Following these chapters, the several oxides are taken up, in so far as practicable, in the order in which they appear in the periodic table. The last four chapters deal with the general theory underlying some of the more important technical applications of the hydrous oxides.

Throughout the volume an attempt is made to correlate systematically and to discuss critically the numerous observations on the colloidal behavior of the hydrous oxides and hydroxides. Emphasis is placed on the part which investigations with these compounds have con-

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tributed to the development of the theories of colloid science and to
the application of these theories in technical practice.   In order to
render the presentation as clear and concise as possible the subject
matter is outlined by the frequent use of section and paragraph
headings.   It is hoped that the book will prove useful as a reference
work alike to those interested in pure science and to those concerned
with its industrial applications, and as a text for the study of colloidal
phenomena in their relation to an important class of inorganic
compounds.

I am grateful to the McGraw-Hill Book Company for permission
to use the term hydrous oxides in the sub-title of this volume.

HARRY BOYER WEISER

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THE HYDROUS OXIDES
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CHAPTER I

HYDROUS OXIDE SOLS AND GELS

The hydrous oxides occur in the colloidal state most frequently in the form of sols and gels. Before considering the general methods of formation and properties of colloidal dispersions of this class of compounds, it seems advisable to define in order the terms which are used in the heading of this chapter.

Terminology

Hydrous Oxide. When a solution of a ferric salt is treated with an alkali, a voluminous, gelatinous precipitate is formed which is commonly called ferric hydroxide and assigned the formula $Fe(OH)_3$. The extent to which this terminology is fixed in our chemical literature is evidenced by its almost universal use in our textbooks, although a half-century ago van Bemmelen[1] showed not only that no definite hydrate of the formula $Fe(OH)_3$ or $Fe_2O_3 \cdot 3H_2O$ exists, but also that no other hydrate is formed by the usual method of precipitating the oxide. The viscous voluminous precipitate when first formed may be represented approximately by the formula $Fe_2O_3 \cdot \pm 20H_2O$, but it loses water, gradually attaining a composition that varies with the time, the temperature, and the pressure of the water vapor in contact with it. A composition corresponding to a definite hydrate is, therefore, purely accidental, depending as it does on the exact method of formation, the method of drying, the temperature, and the age of the sample. Precipitated oxides like ferric oxide which contain varying amounts of water adsorbed by the oxide particles are called hydrous oxides to distinguish them from hydrates in which the water is chemically combined in definite stoichiometric proportions. Some hydrated oxides, such as $Al_2O_3 \cdot 3H_2O$ and $Fe_2O_3 \cdot H_2O$, adsorb varying amounts of water, depending on the conditions of formation. Such preparations are termed hydrous hydrated oxides. By the application of

[1] Rec. trav. chim., **7**, 106 (1888).

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x-ray analytical methods, it has been established in a number of cases that the elements of water are combined in the form of a hydroxide such as $Be(OH)_2$, $Co(OH)_2$, and $Fe(OH)_2$. Gelatinous precipitates of such compounds are called hydrous hydroxides. On standing, the primary colloidal particles of the hydrous oxides and hydroxides grow and lose water spontaneously, causing the mass to assume a less gelatinous and more granular character. This spontaneous transformation from a loose voluminous precipitate to a granular mass is accompanied by a decrease in the solubility, the adsorbability, and the peptizability of the compounds.

Hydrous Oxide Sol. The term sol as applied to this class of compounds usually refers to the dispersions of the hydrous oxide particles in water. Oxide dispersions in organic media are frequently encountered, but in these cases the water adsorbed on the particles is largely displaced by the organic liquid. Dispersions of hydrous oxides in solid media are rare, but anhydrous oxides in the highly dispersed state impart the color to certain glasses and glazes and to natural and synthetic gems.

Hydrous Oxide Gel. Gelatinous precipitates and jellies are the two forms of solid or semi-solid colloids included under the general term gel. Although the rapid precipitation of a hydrous oxide usually gives a gelatinous mass with a supernatant liquid—a gelatinous precipitate—it is frequently possible to bring about uniform precipitation throughout the entire solution with the formation of a jelly which differs from a gelatinous precipitate in that all the liquid is enclosed by the precipitated phase. Jellies of the hydrous oxides such as ferric oxide and chromic oxide, which lose their elasticity and become powdery on drying, are called rigid or non-elastic jellies in contradistinction to the elastic jellies such as gelatin, albumin, and agar which are characterized by perfect elasticity through certain narrow limits and by retaining their elasticity and coherence on drying. In this book the elastic jellies will be taken up only in so far as a consideration of their preparation and properties throws light on the nature of hydrous oxide precipitates.

SOLS

FORMATION

The general methods of forming sols are conveniently classified as condensation and dispersion methods. In the former, smaller particles or molecules are condensed or collected together into particles

of colloidal dimensions; and in the latter, coarse material or aggregates are broken up into units of colloidal size. Both general methods are widely used in preparing sols of the hydrous oxides and hydroxides. The condensation or precipitation methods will be considered first.

Condensation Methods

Von Weimarn's theory of the condensation or precipitation process has been discussed in Volume I, pages 1–4 and 26–28, and will not be reviewed here. In accord with this theory, most of the hydrous oxides are thrown down in a finely divided state even from dilute solution on account of their very low solubility. The problem in the synthesis of their sols consists in preventing the agglomeration of the individual or primary particles into aggregates sufficiently large to settle out. The methods actually employed to prevent agglomeration involve (1) the keeping down of the concentration of coagulating electrolyte either by a suitable choice of reaction or by dilution and (2) the addition of strongly adsorbed protecting agents such as protecting colloids which form a "water-soluble" film around the primary particles and prevent their coalescence. The following general reactions have proved useful in preparing hydrous oxide sols.

Hydrolysis. Just as reduction is the reaction most frequently encountered in the preparation of sols of the elements, so hydrolysis is the reaction most frequently used in preparing the common hydrous oxide sols. This method was first employed a century and a quarter ago by Gay-Lussac,[2] who prepared what we now know to be colloidal alumina by hydrolysis of aluminum acetate. Later, Crum[3] prepared an alumina sol, and Péan de St. Gilles[4] a ferric oxide sol, by hydrolysis of the respective acetates in the hot, followed by boiling which removed the excess acetic acid. In general, the hydrolysis of a salt proceeds further at the boiling point than at room temperature because of the increased ionization of water at the higher temperature. Moreover, the degree of hydrolysis is greater if the resulting oxide is highly insoluble and the acid is weak. On this account acetates are better than halides and nitrates; but the latter salts may be used in certain cases. For example, ferric oxide sol is readily prepared by adding a concentrated solution of ferric chloride[5] slowly to boiling water. The hydrolysis of the dilute solution is practically complete

[2] Ann. chim. phys., **74**, 193 (1810).
[3] Ann., **89**, 168 (1854).
[4] Compt. rend., **40**, 568, 1243 (1855).
[5] Krecke: J. prakt. Chem. (2) **3**, 286 (1871).

at the boiling temperature,[6] but the process is partly reversed in the cold and the acid must be removed by dialysis. Ferric nitrate[7] may be substituted for ferric chloride, but in general, the percentage hydrolysis of the metallic halides and nitrates is so low, except in highly dilute solutions, that, before dialysis, it is necessary to add a base short of precipitation to the salt under consideration (see below). Sulfates cannot be substituted for acetates, nitrates, and halides since the multivalent anions coagulate the sol much more readily than the univalent anions. Sols may be obtained in certain cases by hydrolysis of non-electrolytes such as silicon sulfide,[8] ferric ethylate,[9] and copper succinimide.[10]

Hydrolysis methods have been used in the preparation of hydrous oxide sols of iron, chromium, aluminum, copper, lead, tin, zirconium, thorium, cerium, bismuth, and silicon.

Double Decomposition. Because of the relatively low precipitating power of salts of univalent ions such as sodium chloride, it is possible to prepare most of the hydrous oxide sols by double decomposition reactions involving the use of hydrochloric acid or sodium hydroxide. Thus colloidal silica, stannic oxide, and tungstic oxide may be formed by adding a suitable amount of hydrochloric acid to solutions of sodium silicate, stannate, and tungstate, respectively; and colloidal ferric oxide, chromic oxide, alumina, and stannic oxide may be prepared by adding suitable amounts of sodium hydroxide to solutions of the respective chlorides. If sulfates are used instead of the halides, the amount of alkali which can be added before precipitation is much less because of the flocculating action of the sulfate ions. Under favorable conditions it is possible to add 50 to 75% of the theoretical amount of base to the chlorides before a permanent precipitate is formed. It is common practice in making sols to mix the reacting solution short of precipitation and to remove the salt impurities by dialysis either in the hot or the cold.

Dispersion Methods

General dispersion or peptization methods commonly used in preparing hydrous oxide sols involve (1) the removal of agglomerating electrolytes from the precipitated gel or (2) the addition of a peptizing

[6] Wright: J. Chem. Soc., **43**, 156 (1883).

[7] Scheurer-Kestner: Ann. chim. phys. (3) **57**, 231 (1859).

[8] Berzelius: "Lehrbuch," 3rd ed., **2**, 122 (1833).

[9] Nicolardot: Compt. rend., **140**, 310 (1905).

[10] Ley: Ber., **38**, 2199 (1905); Ley and Werner: **39**, 2178 (1906).

electrolyte to the gel. The method of disintegration by mechanical means is of very limited application.

Removal of Agglomerating Electrolytes. Since freshly formed precipitates of the hydrous oxides consist of a mass of extremely minute primary particles, it is usually possible to peptize the precipitates by washing out the excess of agglomerating electrolyte which is responsible for precipitation in the gelatinous state. The chief electrolytes found in the precipitates are the excess of added base and the salt formed in the metathetical reaction. The ease of peptization depends on the ease with which the agglomerating agents are washed out; hence it is advisable to add as little base, preferably ammonium hydroxide, as possible, and to start with a chloride rather than a sulfate since the latter is adsorbed so much more strongly and gives a denser floc than the former. For example, a sol of hydrous ferric oxide is readily obtained by treating ferric chloride solution with sufficient ammonia to cause precipitation followed by washing the freshly formed gel by decantation preferably with the aid of the centrifuge. Quite pure, stable sols can be obtained by continuing the washing with the supercentrifuge. Thus Bradfield[11] prepared by this method a cherry-red ferric oxide sol containing but 1 equivalent of chlorine to 400 of ferric iron. It is important to work with a fresh gel since aging results in the coalescence of primary particles into agglomerates that are not readily broken up by washing. For the same reason, the more rapidly the freshly formed gel is washed, the more complete will be the peptization by washing.

Addition of a Peptizing Electrolyte. If the coalescence of the primary particles takes place to such an extent that the precipitation is not readily reversible by washing, the desired result may be obtained by the addition of a suitable peptizing electrolyte. This method consists essentially of the following steps: (1) throwing down of the precipitate in the cold from the chloride, nitrate, or acetate solution; (2) washing, preferably by the aid of the centrifuge, until peptization starts; (3) adding just enough of a suitable electrolyte to cause complete peptization; and (4) dialyzing to remove excess electrolyte. Most hydrous oxide gels are peptized by their chlorides, nitrates, and acetates, or by the corresponding acids, to give positively charged sols as a result of preferential adsorption of the common cation or of hydrogen ion. Peptization is accomplished less readily by sulfates and other salts with multivalent anions, since the coagulat-

[11] J. Am. Chem. Soc., **44,** 965 (1922).

ing action of strongly adsorbed anions acts in opposition to the peptizing action of the cations.

Positive sols of all the metallic hydrous oxides have been prepared by suitable adaptations of the above procedure. Frequently the oxides are peptized by the addition of an excess of alkali to give negative sols, as a result of preferential adsorption of hydroxyl ion. For example, hydrous chromic oxide is peptized by a suitable excess of caustic soda and no chromite is present in the resulting negative sol.[12] The more acidic oxides are frequently peptized by very small amounts of base to give negative sols. Thus, Zsigmondy[13] suspended 1.5 g of hydrous stannic oxide in water and effected complete peptization with a single drop of ammonium hydroxide containing but 0.03 g of ammonia. In this case, any excess of peptizing agent may be removed by boiling, thus avoiding the necessity of dialysis.

GELATINOUS PRECIPITATES

FORMATION

Since many of the hydrous oxides are extremely insoluble, they usually separate in a gelatinous form when a base is added to a solution of a metallic salt. This applies to the common oxides such as those of iron, chromium, aluminum, and silicon which always come down in the gelatinous state even from hot dilute solutions and which retain this form for long periods in contact with water. Other oxides such as those of silver and mercury, which possess an appreciable solubility, give flocculent rather than gelatinous precipitates unless the percentage supersaturation is increased enormously by precipitation from concentrated solutions. In certain cases the gelatinous precipitate is a hydrous hydrate or hydroxide rather than a hydrous oxide. Common examples of this are cupric hydroxide, magnesium hydroxide, and ferrous hydroxide. Copper hydroxide loses both its hydrate and gel water on warming, giving a granular precipitate of cupric oxide. Because of the relatively high solubility of calcium and magnesium hydroxides, they yield gelatinous precipitates only when highly concentrated solutions of salt and base are mixed.

STRUCTURE

Although gelatinous precipitates are easily recognized and are readily formed, it is not obvious why they should be gelatinous.

[12] Nagel: J. Phys. Chem., **19**, 331, 569 (1915); Bancroft: Chem. News, **113**, 113 (1916).

[13] Ann., **301**, 361 (1898).

Recent investigations of the physical character of bodies by means of x-rays confirm von Weimarn's contention that many gelatinous precipitates, such as hydrous alumina and ferric oxide, which we used to think were amorphous, consist of myriads of tiny crystals. This naturally raises the question whether the submicroscopic crystals are themselves gelatinous and so impart the gelatinous property to the mass. Unfortunately, von Weimarn does not enlighten us on this point; but it is apparently possible to have gelatinous crystals. Thus Harrison[14] speaks of aqueous solutions of benzopurpurine and chrysophenene setting to jellies containing gelatinous crystals, some of them so fine that they can pass unbroken through a filter paper. Similarly, cholic acid gives a blue precipitate with iodine which may form in clusters of needle crystals possessing rigidity; but under other conditions it may form needle crystals which are gelatinous and can be bent in various shapes by moving the cover glass on the microscope slide. Some of these so-called gelatinous crystals show remarkable vibrations due to the impact of the molecules and move about like the spiral bacteria present on the teeth. Harrison's observations seem to throw some light on the problem of what constitutes a gelatinous crystal or aggregate and hence on the related problem of what is a gelatinous precipitate.

Le Chatelier[15] succeeded in polishing metal with colloidal silicic acid and hence concluded that the gelatinous precipitate consists of anhydrous silica and water. As Bancroft[16] points out, this is not necessarily conclusive because anhydrous silica might have formed as a result of the pressure used in polishing. It now appears, however, that Le Chatelier was correct in his original conclusion although his evidence was open to question. In this same connection Zsigmondy[17] explains the liquid character of gels rich in water by assuming the ultramicrons to be surrounded by a water layer and to have a certain free path and motion. The objection to this view is that Zsigmondy does not show why it should be so. Harrison's observations on gelatinous crystals bear on this point. Gelatinous crystals are apparently extremely fine, needle-shaped masses so thin that they lack rigidity and so flexible that they can be bent and twisted into various shapes and may move under the bombardment of water molecules. A cluster or network of such needle-shaped, flexible

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[14] "The Physics and Chemistry of Colloids," Faraday Soc. Rept., 58 (1920).
[15] "La silice et les silicates," 76 (1914).
[16] "Applied Colloid Chemistry," 236 (1921).
[17] Zsigmondy-Spear: "Chemistry of Colloids," 138 (1917).

crystals that adsorb water strongly would form a viscous or plastic mass, usually known as a gelatinous precipitate. If the crystals are compact and rigid rather than thin and flexible, they would not form a gelatinous precipitate unless they united into threads or strings possessing the flexibility and elasticity which characterize a thin needle crystal. Obviously the particles need not be crystalline, and in some cases they probably are not. A gelatinous precipitate is apparently a network composed of extremely finely divided particles which have coalesced to form flexible filaments or chains and which adsorb water very strongly and so are highly hydrous. Where the particles do not adsorb water particularly strongly and where. the tendency to coalesce into filaments or threads is not great, a high concentration of the finely divided particles is necessary, as in calcium carbonate and barium sulfate. Since neither tendency is very marked in metals such as gold, gelatinous precipitates of gold are obtained only under special conditions. On the other hand, platinum black adsorbs water rather strongly and gives a gelatinous precipitate when thrown down rapidly by the reduction of a sodium chlorplatinate solution with sodium formate. Indeed, Benton[18] once prepared a platinum jelly in this way. Similarly, Börjeson[19] in Svedberg's laboratory prepared a cadmium jelly by allowing a very dilute sol of cadmium in alcohol to stand for some time in a glass bottle. In this case the particles were only 5 mμ in radius and the cadmium concentration but 0.2 to 0.5%.

Conclusive visual evidence of the structure of gelatinous precipitates was obtained by Weiser and Cunningham[20] in the course of an ultramicroscopic study of the various types of sulfur precipitates which are formed by coagulation of Selmi's sulfur sol with different electrolytes (Vol. I, p. 338). Thus reversible, gelatinous precipitates result on precipitating the sol with strongly hydrated lithium or sodium ion, and plastic, irreversible flocs with the weakly hydrated potassium or barium ion. Ultramicroscopic observation of the gelatinous clumps shows them to consist of an agglomerate of ultramicroscopic particles surrounded by an envelope of water. The film of adsorbed water, together with the water entrained during the agglomeration process, gives a flexible hydrous mass, the gelatinous precipitate. Ultramicroscopic observations of the change taking place when a weakly adsorbed highly hydrated cation is removed

[18] J. Phys. Chem., **30**, 1415 (1926).

[19] "The Physics and Chemistry of Colloids," Faraday Soc. Rept., 55 (1920).

[20] J. Phys. Chem., **33**, 301 (1929); Colloid Symposium Monograph, **6**, 319 (1928).

from a gelatinous sulfur clump by displacing it with a more strongly adsorbed, less hydrated cation, reveal a marked shrinkage as the result of loss of adsorbed water and the coalescence of the particles giving a ball of sulfur which may occupy a volume not more than 1/500 that of the original clump. Motion pictures taken of this change in the physical character of the clumps disclose clearly the optical effects produced by the outflow of the adsorbed and entrained water and the coalescence of the ultramicrons.

JELLIES

STRUCTURE

The most widely accepted theories of jelly structure are alike in picturing the bodies as two-phase solid-liquid systems; but there has long existed a fundamental difference of opinion as to the exact nature of the solid framework which is assumed to entrain the liquid phase and the manner in which this framework is formed. One theory assumes that both phases are continuous, the solid phase forming a kind of enmeshing network or sponge which holds the liquid phase; the second theory postulates that the solid phase only is continuous, forming a cell-like or honeycomb framework which holds the liquid phase. These will be considered in order.

The Micellar or Sponge Theory

Since one may precipitate certain oxides and salts in either a gelatinous or a jelly-like form by suitable variations in conditions, it would seem to follow that the structure of the two types of inorganic gels is essentially the same. From this point of view an aqueous inorganic jelly consists of myriads of highly hydrous or gelatinous particles enmeshed into a network or sponge which entrains all the liquid phase.

This concept of the structure of inorganic jellies is essentially the same as the micellar theory of the structure of the organic jellies proposed by Frankenheim[21] and Nageli.[22] According to this the earliest theory of jelly structure, distensible bodies such as gelatin, agar, and rubber are assumed to consist of small, anisotropic, crystal-like, molecular aggregates which retain their identity even when the substance goes into (colloidal) solution. The micelles, as Nägeli

[21] "Die Lehre von der Kohäsion," Breslau (1835).
[22] "Pflanzenphysiologischen Untersuchungen," Zurich (1858); "Theorie der Gärung," Munich (1879).

called the molecular aggregates, take up water in such a manner that they are surrounded by a water layer, the thickness of which is determined by the relative intensity of the attraction of the micelles for water and for each other. Zsigmondy's earliest investigations with the ultramicroscope led him to conclude with Nägeli that the jelly structure is granular or flocculent; but later, Zsigmondy and Bachmann[23] observed a fibrilar structure in addition to the apparently grainy structure encountered in diluted gels of gelatin, agar, and hydrous silica. The fibrils or threads are quite sharply defined in soap jellies studied by Bachmann and later by McBain and his coworkers[24] and in barium malonate jellies studied by Flade.[25] The latter noted the crystalline character of the fibrils and suggested that jellies in general probably consist of a network of crystalline threads.[26] Gortner[27] prepared a jelly of di-benzoyl-l-cystine which was found to consist of minute crystalline, needle-like fibrils. Büchner[28] showed that jellies, obtained from myricyl alcohol dissolved in chloroform and in amyl alcohol, consist of a conglomerate of very fine crystals which retain a large amount of liquid in the meshes.[29] Bradford[30] champions the theory that the reversible sol-gel transformation is merely an extreme case of crystallization. Ultramicroscopic examination of a gelatin jelly reveals the presence of spherites which Bradford believes to be made up of crystalline particles. Moeller[31] likewise believes gelatinization to be a kind of crystallization in which a lattice of crystal threads is formed that entrains the liquid; and von Weimarn[32] concludes from his investigations that a jelly is a sponge composed of highly dispersed crystalline granules soaked in dispersive medium.

Although the solid phase in many jellies is definitely crystalline, this does not mean that there is no such thing as an amorphous precipitate of the gelatinous or jelly-like type. The theory that

[23] Kolloid-Z., 11, 150 (1912).

[24] Laing and McBain: J. Chem. Soc., 117, 1506 (1920); Darke, McBain, and Salmon: Proc. Roy. Soc. (London) 98A, 395 (1921).

[25] Z. anorg. Chem., 82, 173 (1913).

[26] Cf. Stübel: Pflügers Arch., 156, 361 (1914); Howell: Am. J. Physiol., 40, 526 (1916).

[27] Gortner and Hoffman: J. Am. Chem. Soc., 43, 2199 (1921).

[28] Rec. trav. chim., 42, 787 (1923).

[29] Cf. Fischer and Bobertag: Jahresber. schles. Ges. vaterl. Kultur, 86, 33 (1908); Chem. Zentr., (I) 262 (1909).

[30] Biochem. J., 12, 351 (1918); 14, 91 (1920); 15, 553 (1921).

[31] Kolloid-Z., 23, 11 (1918).

[32] J. Russ. Phys.-Chem. Soc., 47, 2163 (1915).

jelly formation is merely a process of crystallization seems to be contradicted by the work of Bogue,[33] McBain,[24] and Barratt,[34] although all of the latter are strong supporters of a filamentous structure.

Even though it is possible for colloidal particles to possess the thread-like characteristics essential for forming an entangling mesh in which each particle is discrete, it seems more probable that in most cases the micelles actually become stuck together or oriented into loose aggregates which may take the form of chance granules, threads, or chains. Such a linking together of the particles to form an enmeshing network seems essential in some of the extremely dilute hydrous oxide jellies to which we shall refer later on. Laing and McBain[35] consider the gelatinization of soap to result from the linking up of colloidal particles to form a filamentous structure. "The colloidal particles in soap and gel are the same; but whereas in the former they are independent, in a fully formed gel they become linked up probably to form a filamentous structure." The formation of the soap curd is looked upon as a phenomenon analogous to crystallization that is distinct from the process of jelly formation.[36]

The conception of micellar orientation in the process of gelation is supported by a number of observations mentioned by Laing and McBain, among which are the following: the identity in sol and gel of the electrical conductivity,[37] and the lowering of the vapor pressure; the intensifying of the molecular movement by heat which overcomes the forces holding the particles and causes melting of the gel; the transformation of certain jellies, such as nitrocotton, into sol, by mechanical stirring which breaks down the orienting bonds between the particles;[38] the absence of Brownian movement in soap or gelatin jellies;[39] the dependence of the apparent viscosity of sols on previous treatment and history which influence the degree of orientation of their particles;[40] the tendency of the jelly structure to shrink and exude liquid—synerize—as a result of the component of attraction in the orienting force between the particles; and the frequent occurrence of supersaturation and hysteresis with regard to

[33] Chem. & Met. Eng., 23, 61 (1920); J. Am. Chem. Soc., 44, 1343 (1922).
[34] Biochem. J., 14, 189 (1920).
[35] J. Chem. Soc., 117, 1506 (1920); Nature, 125, 125 (1930).
[36] Cf. Piper and Grindley: Proc. Phys. Soc. (London) 35, 269; 36, 31 (1923).
[37] Cf. Arrhenius: Öefvers. Stockholm Akad., 6, 121 (1887).
[38] Cf. Alexander: "Glue and Gelatin," 75 (1923).
[39] Bachmann: Z. anorg. Chem., 73, 125 (1911).
[40] Cf. Hatschek: Kolloid-Z., 13, 88 (1913).

gelation. To these should be added the observation of Walpole[41] that the refractive index of a gelatin-water system is a linear function of the concentration, and when plotted against the temperature, no break occurs at the point of gelation; and the findings of Bogue[33] that the viscosity-plasticity change in the sol-gel transformation is gradual and regular.

In certain starch-water jellies, Meyer[42] observed a net structure made up of turbid drops or globules. In some of them the visible globules are not in apparent contact, but in such cases it is altogether probable that the larger ones are held together by smaller ones that are invisible under the conditions of the experiment. Similarly, a net structure made up of globules rather than filaments has been observed with gelatin in aqueous alcohol.

The Cellular or Honeycomb Theory

From extended investigations first on foams and emulsions and later on jellies of gelatin, agar, and hydrous silica, Butschli[43] concluded that in jellies the droplets of liquid are held in pockets in a cell-like framework comparable to a honeycomb, an idea suggested, in all probability, by the cellular structure of the stems of young plants which enclose a relatively high percentage of water and still possess considerable rigidity. The walls of the cells in a silica jelly appeared to be about 0.3 μ in diameter and the pockets which held the liquid from 1 to 1.5 μ in diameter. Gelatin jellies that appeared homogeneous under the microscope were hardened with alcohol or chromic acid to make their structure visible, and these likewise appeared to be made up of thin films.

Butschli's general concept of jelly structure was supported by van Bemmelen,[44] Quincke,[45] and Hardy.[46] According to the latter, gelatin consists of two phases separated by a well-defined surface: one phase a solid solution of gelatin in water and the other a solution of water in gelatin. Like van Bemmelen, he assumes that both phases are liquid at first; but with fall of temperature, one becomes solid. The solid solution forms on the concave side of the surface of separation when the proportion of gelatin is small, and on the convex side when the proportion of gelatin is large. In the

[41] Kolloid-Z., **13**, 241 (1913).
[42] Kolloid-Beihefte, **5**, 1 (1913).
[43] "Untersuchungen uber Strukturen," Leipzig (1898).
[44] Z. anorg. Chem., **18**, 14 (1898).
[45] Ann. Physik (4) **9**, 793, 969 (1902); **10**, 478, 673 (1903).
[46] Z. physik. Chem., **33**, 326 (1900).

latter case the drops of liquid are held in a solid gelatin-rich phase. As Bancroft[47] points out, such a jelly consists merely of a viscous medium in which liquid is dispersed and so does not have a honeycomb structure in the same sense that an emulsion has a honeycomb structure. "It is probably better to reserve the term 'honeycomb' for structures in which the cell walls are thin relatively to the diameter of the cells and it may be desirable to restrict it to cases like the emulsions where there is a distinct film around the drops."[48]   Bancroft subscribes to the sponge theory of jelly structure but he believes that both phases in a gelatin jelly are colloidal.   "Since water peptizes gelatin under certain conditions, there is no reason why liquid gelatin or a gelatin-rich phase should not peptize water.   It is possible therefore that with gelatinous precipitates and with jellies we have a binary system in which each constituent peptizes the other."

The investigations of Butschli, van Bemmelen, and Hardy seemed so conclusive that for many years the honeycomb theory was generally looked upon as established.[49]   But later investigations of Zsigmondy and his pupils disclosed errors in the optical observations of Butschli and Hardy and showed that the heterogeneity of jellies was of an entirely different order of magnitude from that which the latter supposed.   By applying the laws of capillarity to van Bemmelen's[50] results on the hydration and dehydration of silica gel, Zsigmondy[51] estimated the diameter of the pores to be 5 mμ, which is 200 or 300 times smaller than Bütschli observed.   This was confirmed by Anderson,[52] who showed that the pores vary in size, some being as small as 2 mμ in diameter.   Working by the same method, Bachmann[53] found that gelatin jellies hardened by alcohol or chromic acid contained very much finer spaces than Bütschli supposed.[54]   Apparently the structures observed by Bütschli and Hardy were artifacts produced by the action of the hardening agents on the much finer structure already existing.[55]

[47] "Applied Colloid Chemistry," 241 (1921).

[48] Bancroft: "Applied Colloid Chemistry," 3rd ed., 339 (1932).

[49] *Cf* Freundlich: "Kapillarchemie," 475 (1909).

[50] "Die Absorption," 198 (1910).

[51] Z. anorg. Chem., **71**, 356 (1911).

[52] Z. physik. Chem., **88**, 191 (1914).

[53] Z. anorg. Chem., **100**, 1 (1917).

[54] *Cf., also,* Kraemer: J. Phys. Chem., **29**, 1523 (1925).

[55] *Cf.* Pauli: "Der kolloidale Zustand und die Vorgänge in der Lebendigen Substanz," Braunschweig (1902); Fischer: "Fixerung, Färbung, und Bau des Protoplasms," 312 (1899).

Summary

Whatever may be the exact nature of jellies, the experimental evidence indicates that most of them possess a sponge structure rather than a honeycomb structure. This is especially true of the inorganic jellies. The presence of definite threads or filaments leaves little room to doubt the existence of an interlacing network structure in certain jellies. It would, of course, be highly interesting if jellies of widely different substances were all essentially identical in structure. Such a condition seems altogether unlikely; but investigators have apparently sought to establish such an identity. Studies on specific jellies have led some to conclude that all jellies are made up of a framework of amorphous threads; others, that they are composed of crystalline threads; and still others, who fail to find any threads or filaments at all but observe an irregular grouping of particles. Doubtless all are right in specific cases. Indeed, it is not unlikely that there are various arrangements of molecular aggregates in different jellies and perhaps in the same jelly. In a heterogeneous mixture of complex groups such as are found in gelatin sol or jelly, it is probable that the process of gelation and the jelly structure are more complex than in the inorganic jellies or in soap jellies. The orientation of the particles may result in fibrils in certain instances and in more or less irregular arrangements in others. In some the fibrils may consist of definite crystals, whereas in others the crystalline characteristics may be entirely lacking. In all cases it seems probable that the particles are highly hydrous as a result of adsorption or absorption and that they are linked together, forming an irregular mesh or network in the interstices of which liquid is entrained.

PREPARATION OF HYDROUS OXIDE JELLIES

If we start out with the assumption that a gel consists of myriads of particles enmeshed into a network which entrains liquid, it follows that any substance should form a gel, provided a suitable amount of a highly dispersed substance is precipitated and provided the particles adsorb the dispersing medium very strongly. The amount of the dispersed phase that must be present to form a firm jelly by a precipitation method will depend on the size and nature of the orientation of the particles and the extent to which they adsorb the dispersing liquid. Many of the typical elastic organic jellies are best prepared either by swelling in a suitable liquid or by preparing a sufficiently

concentrated sol in the hot and allowing it to cool. These methods are not applicable to the preparation of inorganic jellies, of which the oxide jellies are typical. The general procedures for preparing the latter will be considered in order.

Precipitation of Sol. Since finely divided particles that adsorb water strongly are of primary importance for the formation of hydrous jellies, it would seem that the most promising method of preparing jellies with a low ratio of solid to liquid phase would be to precipitate hydrous substances from colloidal solution. Von Weimarn's precipitation theory would tell us, of course, that this precipitation would have to take place at a suitable rate under conditions that are not conducive to growth of the individual particles; but it does not enable us to predict the optimum rate of coagulation, the effect of salts on jelly formation, or the conditions that favor the formation of a jelly rather than a gelatinous precipitate. As a result of investigations in the author's laboratory on the formation of typical dilute inorganic jellies, of the hydrous oxides particularly, it is possible to outline the general conditions of jelly formation and the effect on the process of various factors other than the percentage supersaturation "at the important first moment of the first stage of condensation"[56] from molecules to invisible particles. Jellies would be expected to form from colloidal solution if a suitable amount is precipitated at a suitable rate without agitation in the absence of a medium that exerts an appreciable solvent or peptizing action. If the concentration of the colloid is too low, no jelly or only a very soft jelly can result. If the velocity of precipitation is too great, contraction is likely to occur with the formation of a gelatinous precipitate instead of a jelly. The effect of the presence of salts on jelly formation is, therefore, determined in large measure by the precipitating and stabilizing action of the ions in so far as these affect the rate of precipitation. In general, a slow rate of precipitation favors the formation of a uniform jelly rather than a gelatinous precipitate, provided there is little or no tendency of the particles to grow as a result of the solvent action of the electrolyte. The favorable concentration for different electrolytes is in the immediate region of their precipitation concentration. A little below this value, no precipitation or only a slight precipitation takes place; whereas above this value, coagulation is usually so rapid that a gelatinous precipitate is formed instead of a jelly. The reason is that time is not allowed for the uniform mixing of the colloid with

[56] Von Weimarn: *cf.* Vol. I, p. 1.

coagulant, and the slow uniform precipitation necessary for the building of a uniform jelly structure is replaced by rapid uneven coagulation and the consequent contraction that distinguishes a gelatinous precipitate from a jelly.

The accuracy of these deductions has been demonstrated repeatedly, and frequent reference will be made to them in later chapters. In many cases, these jellies may be obtained in relatively low concentrations. A notable example is the case of hydrous chromic oxide which formed a firm jelly containing but 0.18% chromic oxide and a soft jelly containing 0.09% chromic oxide.[57] The formation of such dilute jellies can result only when the particles are very hydrous and when the conditions of precipitation allow time for the building up of an enmeshing network. If the particles are but slightly hydrous and show but little tendency to link together into threads, extremely high concentrations must be present, as von Weimarn found.

Prakash[58] minimizes the importance of slow coagulation or precipitation on the ground that certain jellies form quite rapidly. Slow precipitation or coagulation is desirable, however, for the formation of uniform jellies even when the substance always gives a jelly-like precipitate and it is absolutely essential for the formation of dilute jellies when the tendency to precipitate as a jelly is not very great. As a result of viscosity measurements during the formation of jellies Prakash[59] postulates an increase in surface hydration (adsorption) accompanying the lowering of the charge on the particles. He therefore distinguishes between the effect of this alleged surface hydration and the effect of the formation of a structure during the coagulation process. Even if one is willing to accept the theory that both surface hydration and structural changes bring about the increased viscosity during the coagulation process, few people will agree that Prakash has succeeded in distinguishing between the two factors experimentally.

Dialysis of Sol. Prolonged dialysis of colloidal solutions frequently leads to the precipitation of a part of the suspended phase as a gelatinous precipitate. When this process was carried out in a suitable way on a colloidal solution of ferric arsenate peptized by ferric chloride, Grimaux[60] obtained a firm, transparent jelly. This observation has been confirmed and extended by Holmes and his

[57] Weiser: J. Phys. Chem., **26**, 409 (1922).

[58] J. Indian Chem. Soc. (Ray Commemoration Volume) 99 (1933).

[59] Kolloid-Z., **60**, 184 (1932); J. Soc. Chem. Ind., **50**, 387T (1931).

[60] Compt. rend., **98**, 1540 (1884).

pupils.[61] Similar observations have been made in the author's laboratory with hydrous oxides of chromium and aluminum, and the method is probably a general one. From the point of view outlined in the foregoing section, the formation of jellies by dialysis of a colloidal hydrous substance is readily understood. Dialysis merely removes the stabilizing ion slowly and uniformly below the critical value necessary for peptization; and precipitation results just as if the adsorption of the stabilizing ion were compensated for or neutralized by the addition of an electrolyte having a suitable precipitating ion. The accuracy of these deductions has been demonstrated conclusively in a series of investigations on the arsenates of iron and aluminum.[62]

Precipitation from Solution. Because of the very low solubility of most of the metallic oxides, a high percentage supersaturation (P/L value, to use von Weimarn's formulation) prevails on mixing even dilute solutions of the respective salts and base. Under these conditions there is a rapid formation of extremely minute hydrous nuclei. If the concentration of the reacting solutions is relatively low, a gelatinous precipitate is obtained; but if the concentration is sufficiently high, a semisolid mass results that entrains all the liquid phase, thus forming what has been termed a jelly. Such relatively concentrated jellies usually bear little resemblance to the dilute transparent jellies formed by precipitation of sol since the former are, as a rule, non-uniform translucent masses containing bubbles of air entangled during the mixing process.

As already indicated, gelatinous precipitates usually form on mixing dilute solutions which precipitate immediately (P small, and L very small); but a jelly is seldom obtained under these conditions. The reason is evident when we consider the impossibility of getting the instantaneous mixing of the solutions which is essential for uniform precipitation throughout the mixture. One part is precipitated before another is mixed with the precipitant, and the uniformity characteristic of a jelly is lost. Moreover, the mixing itself will tend to destroy the jelly structure. The results are, therefore, not unlike those obtained when a colloid capable of forming a jelly by slow precipitation is coagulated too rapidly by the addition of excess electrolyte. To obtain a jelly from a colloidal solution, it is necessary to add such an amount of electrolyte that thorough mixing is possible before

[61] Holmes and Rindfusz: J. Am. Chem. Soc., **38**, 1970 (1916); Holmes and Arnold: **40**, 1014 (1918); Holmes and Fall: **41**, 763 (1919).

[62] Weiser and Bloxsom: J. Phys. Chem., **28**, 26 (1924).

appreciable coagulation takes place. From these considerations, it follows that precipitation of a hydrous substance as a result of double decomposition might form a jelly instead of a gelatinous precipitate if the thorough mixing of the solutions could be effected before precipitation began and if the precipitation, once started, proceeded at a suitable rate. Such conditions do not obtain as a rule but they are entirely possible theoretically. Thus the precipitation may·be the result of a stepwise process, one step of which proceeds at a suitably slow rate. It is further possible to have a reaction that goes very slowly at low temperatures but with marked velocity at higher temperatures. This would not only allow of mixing without precipitation but would also enable one to control the subsequent rate of reaction by a suitable regulation of the temperature. Such a favorable combination of circumstances obtains when a manganese salt of a strong acid and KH_2AsO_4 are mixed.[63] Similarly, the rate of precipitation of hydrous silica from silicate of soda can be adjusted to give a uniform, perfectly transparent jelly by suitable regulation of the concentration, pH value, and temperature of the interacting solutions (p. 193).

Favorable conditions for the precipitation of a jelly may be realized by the slow hydrolysis of a suitable salt. Thus if a solution of aluminum sulfate is poured on a few iron turnings, slow hydrolysis takes place, with the ultimate formation of a firm hydrous aluminum oxide jelly.[64]

GENERAL PROPERTIES OF HYDROUS OXIDE GELS

Dehydration Isotherms and Isobars

The systems hydrate-oxide (or lower hydrate)-water vapor and oxide-water vapor both consist of two components; application of the phase rule shows that the first is a univariant and the second a bivariant system. Typical isotherms and isobars are shown by the unbroken curves in Fig. 1, A and B, respectively. I is typical of definite hydrates like $MgO \cdot H_2O$ or $Mg(OH)_2$ which undergo reversible dehydration. The hydrous hydrates such as $Al_2O_3 \cdot 3H_2O$, $WO_3 \cdot H_2O$, etc., in general, do not rehydrate after decomposition and give isotherms and isobars without sharp breaks as shown by II. The rounded corners result from variations in particle size, lattice distortion, and lattice strain. Complications may arise in the interpretation of dehy-

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[63] Deisz: Kolloid-Z., **14**, 139 (1914); Weiser and Bloxsom: J. Phys. Chem., **28**, 39 (1924).

[64] Cushman and Coggeshall: Trans. Am. Electrochem. Soc., **39**, 81 (1921).

dration curves for hydrous hydrates if the product of dehydration is a powerful desiccating agent. This will be discussed in connection with the hydrates of alumina (p. 94). III is typical of the hydrous oxides such as ferric oxide, chromic oxide, and titanium dioxide in which the water is not held in a definite ratio but varies continuously with the vapor pressure. The curves for silica and tantalia differ from III in exhibiting a point of inflection at some point which varies with the method of preparation and treatment of the sample. This
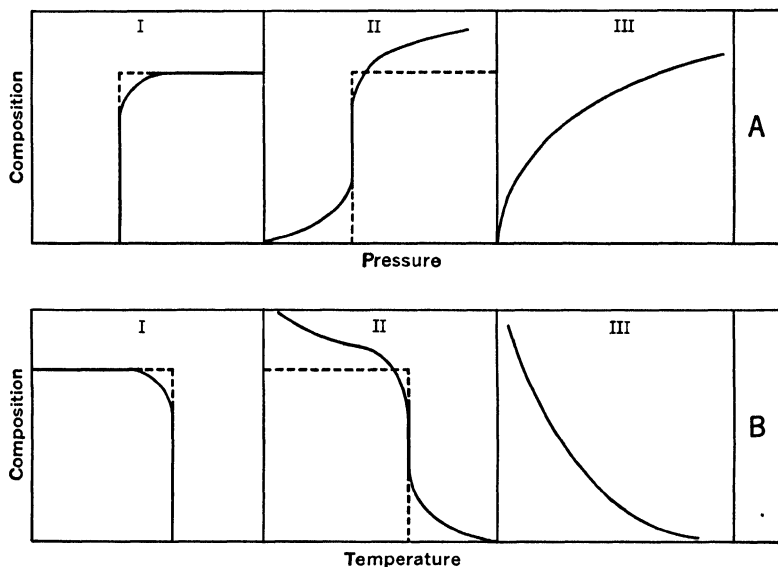
Fig. 1.—Typical dehydration curves: (A) Isotherms; (B) Isobars.

phenomenon will be considered in detail in the chapter on hydrous silica (p. 196).

To account for the absence of sharp breaks in the dehydration curves for a crystalline hydrate, Hüttig[65] assumes that only a part of the hydrate water is held definitely in place in the crystal lattice, while a part may move about with more or less freedom. This water which is assumed to have a certain freedom of movement is termed by Hüttig[66] " osmotically bound " water to distinguish it from water chemically combined or water held in capillaries or adsorbed on the surface of the solid phase. The term osmotically bound water origi-

[65] Fortschr. Chem., Physik, physik. Chem., **18**, 5 (1924).
[66] Kolloid-Z., **58**, 44 (1932).

nated as a result of the observation that a number of the hydrous oxides give dehydration isobars like III B, which can be represented by an equation similar to van't Hoff's osmotic pressure law which states that solutions of equal volume, equal temperature, and equal osmotic pressure contain the same number of molecules. By eliminating the osmotic pressure the van't Hoff equation takes the form

$$\ln \frac{p_0}{p} = \frac{n_1}{n}$$

in which p_0 is the vapor pressure of pure water; p, the vapor pressure of the solution at the same temperature; n_1, the number of dissolved molecules and; n, the number of molecules of the solvent.

For the univariant oxide-water systems which give dehydration curves like III B, the value of n might be set equal to 1 since the amount of the dry solid phase is constant. It was found, however, that in order to make the equation fit, it was necessary to multiply the number of molecules of dry solid ($= 1$) by an association or dissociation factor, k. The osmotic law equation thus takes the form

$$\log \frac{p_0}{p} = \frac{k}{n}$$

where p_0 is the vapor pressure of pure water which is a function of the temperature; p, the constant vapor pressure at which the dehydration is carried out; n, the water content of the solid phase; and k, a constant. Applying this equation, the value of k has been found to be constant and equal to approximately 4 for the dehydration of hydrous zirconia and of hydrous thoria; 2, for hydrous titania; 3, for certain hydrous ferric oxides; 1, for hydrous lead peroxide; 3 or 7, for white hydrous tungstic oxide; etc. On the basis of these observations it was assumed that the water is osmotically bound by the solid phase. This means that oxide-water systems which obey the modified osmotic law are in reality solid solutions in which the water is free to move about in the solid phase. Hydrous oxide gels like alumina, chromic oxide, certain samples of ferric oxide, etc., which give dehydration isobars that do not obey the modified osmotic equation, are assumed to be mixed types in which only a part of the water is osmotically bound, the remainder being held in capillaries or adsorbed on the surface of the solid phase. Similarly, a definite crystalline hydrate like yellow tungstic oxide monohydrate which gives a dehydration isobar like II B, instead of sharply defined steps, is assumed to be a mixed type in which a part of the hydrate water is chemically bound

in the orthodox sense and a part is free to move throughout the crystal lattice of the solid phase.

Although Hüttig has shown that the dehydration isobar of certain hydrous oxides may be represented approximately by a modified form of the osmotic equation, it does not follow that in such cases the water is in solid solution in the oxide. In the first place, one would expect to get the same general type of isobar for the gradual loss of adsorbed water with rising temperature. Moreover, many typical hydrous oxides give dehydration isobars of the same general form which do not fit the modified osmotic equation. And finally, if the water is in solid solution it is not obvious why the modified osmotic equation will fit the dehydration isobar of one sample of ferric oxide gel and not of another. Until more conclusive evidence is available, the author prefers to regard curves of the general form of III *B* as adsorption isobars rather than as solid solution isobars.

Aging

For want of a better term, aging signifies the changes in properties which a freshly formed hydrous oxide gel undergoes on standing. In general, the newly formed gel is very highly hydrous, is easily dissolved or peptized by certain dilute oxides and alkalis, shows a high adsorption capacity for ions, and gives no x-ray diffraction pattern or a very diffuse one. On standing at room temperature, the gel gradually becomes less hydrous; the solubility, peptizability, adsorption capacity, and catalytic activity decrease in many cases; and interference lines appear in the x-radiogram. This gradual change in properties is frequently attributed to a transformation from one allotropic modification to another, but more often it is due to growth and agglomeration of minute particles into larger granules and agglomerates with a consequent decrease in specific surface. The absence of interference lines in the x-radiogram of a freshly formed gel, and their appearance with gradually increasing sharpness in the aged gel, are probably due in some instances to an actual change from the amorphous to the crystalline state; but usually the appearance of lines is the result of a gradual increase in crystal size from crystallization centers too small to show a pattern to crystals large enough to diffract the x-rays. Certain hydrous oxides such as chromic oxide give no x-ray interference pattern even on aging for years at ordinary temperatures, but they exhibit all the other changes in properties which are associated with the loss in specific surface accompanying the growth and agglomeration of the minute particles which precipitate initially.

Color is another property which alters with the age of certain precipitated oxides. Thus freshly formed chromic oxide is variously described by different people as bluish, violet-blue, clear blue, clear gray-blue, and gray-violet, the shade differing somewhat depending on whether it is precipitated from a green or violet chromic salt. On aging and drying under suitable conditions the color changes to a distinct green. Similarly, freshly formed hydrous ferric óxide is brown but on aging the color changes to a brick red. No hydrate is formed in either case; the color change results from growth and agglomeration of particles and the loss of adsorbed water.

The Glow Phenomenon

Many freshly formed hydrous oxides, when heated rapidly to temperatures around 500°, evolve enough heat. to cause the whole mass to become incandescent. This behavior which may be termed the glow phenomenon disappears on allowing the oxide to stand and is not observed if the precipitate is heated too slowly. The glow is regarded by some[67] as an accompaniment of the transformation of one allotropic modification of the oxide to another; but this seems unlikely, since the glowing depends on the rate of heating[68] and since the glow temperature varies with the size of the particles. Böhm[69] suggests that it involves a transformation from an amorphous to a crystalline form, but crystalline hydrous ferric oxide having the hematite structure exhibits the phenomenon (p. 35). Wöhler[70] found that the glowing is increased by all conditions which favor hydrosol formation in the preparation of the oxide: for example, the use of dilute reagents, the use of chloride rather than sulfate, and of potassium hydroxide rather than ammonium hydroxide. Moreover, the glow was found to be greater, the greater the adsorption capacity of the precipitate, indicating that the phenomenon is connected closely with the surface area. Under the same conditions of heating, the heat evolved by 1 g of oxide was sufficient to raise its temperature anywhere from 50 to 100° depending altogether on the extent of surface.

In the light of Wöhler's observations, there is little doubt but that the glow is due to a very sudden decrease in the large surface of the

[67] Moissan: Bull. soc. chim. (2) **34,** 70 (1880); Ann. chim. phys. (5) **21,** 199 (1880); Le Chatelier: Bull. soc. chim. (2) **47,** 303 (1887); Mixter: Am. J. Sci. (4) **26,** 125 (1908); **39,** 295 (1915).

[68] Siewert: Jahresber., 243 (1861); cf. Mixter: Am. J. Sci. (4) **26,** 125 (1908).

[69] Z. anorg. Chem., **149,** 219 (1925).

[70] Kolloid- Z., **11,** 241 (1912); Endell and Rieke: Centr. Mineral., Geol., 246 (1914).

oxides prepared by precipitation. The oxides thrown down under different conditions vary in the size of the particles and the amount of enclosed water and hence in the extent of surface. The maximum glow and heat evolution are obtained when the sample, made up of finest particles, is heated rapidly to the glow temperature, which is in the neighborhood of 500°. If a fine-grained precipitate is heated very slowly or kept for some time below the glow temperature, there is a gradual, instead of a sudden, diminution of surface, which is not accompanied by incandescence. Thus, glowing at elevated temperatures is the visible manifestation of the coalescence of primary colloidal particles into larger masses, involving a marked decrease in specific surface.

The Reversible Sol-gel Transformation—Thixotropy

The reversible transformation from a sol to a jelly is readily accomplished in a system like gelatin and water by varying the temperature. It is well known that a gelatin jelly will liquefy when warmed and will set again when cooled, the transformation temperature depending on the concentration. Thus a 1% sol of pure gelatin sets at around 10°, but above 35°, gelation does not take place at any concentration. Since a jelly appears to consist of a network of adhering granules or filaments, it should be possible at constant temperatures to convert a jelly into a sol by shaking or stirring to break up the network structure; and the resulting sol should set again to a jelly on standing provided the particles will coalesce once more to give the enmeshing network structure. As a matter of fact, this has been observed especially with certain hydrous oxide jellies. The phenomenon was termed thixotropy by Freundlich,[71] who has investigated it extensively. Attention was first called to this behavior in ferric oxide jellies made by adding just enough electrolyte to 6–10% Graham sols (p. 48) to cause coagulation. On stirring or shaking such jellies, sols are formed which set again on standing quietly. The shaking merely destroys the loose network structure of the jelly which subsequently re-forms so that the phenomenon can be repeated any number of times. Ultrasonic waves liquefy jellies of alumina, ferric oxide, and gelatin, and cause silica jelly to lose its elasticity temporarily.[72]

Among the hydrous oxides that have been found to give thixo-

[71] "Kapillarchemie," 3rd ed., 2, 616 (1932); Péterfi: Arch. Entwicklungsmech. Organ., 112, 660 (1927).
[72] Freundlich, Rogowski, and Söllner: Kolloid-Beihefte, 37, 223 (1933).

tropic jellies are alumina, titania, zirconia, scandium oxide, vanadium pentoxide, and stannic oxide. It is probable that most jellies could be made to exhibit the phenomenon if there were any point in working out the necessary conditions. Even certain gelatin jellies will liquefy reversibly if shaken soon enough after setting before the structure has become too firmly fixed.[73]

Diffusion in Jellies—The Liesegang Phenomenon

The rate of diffusion of electrolytes in dilute jellies is almost the same as in pure water; but in concentrated jellies it is much slower. A number of interesting reactions have been carried out in transparent jellies such as gelatin and silica jellies. The usual method of procedure consists in adding one electrolyte to the solution before the jelly sets, after which a solution of a second electrolyte is poured on the jelly and allowed to diffuse into the mass where interaction takes place. If a crystalline precipitate is formed by the reaction, the crystals will be much larger and better formed than if the solutions are mixed directly. For example, large gold crystals result by reducing gold salts in silica jelly with a number of reducing agents. The function of the jelly is to prevent rapid mixing of the reacting solutions thereby avoiding rapid precipitation and the consequent formation of amorphous particles or small crystals.

Reactions in jellies sometimes lead to the formation of the so-called Liesegang rings or rhythmic bands of precipitates, instead of large crystals. The phenomenon was discovered by Liesegang,[74] who placed a drop of silver nitrate on a glass plate coated with moist gelatin containing potassium dichromate, and obtained a series of concentric rings of silver chromate. If the reaction is carried out in a test tube, a series of parallel bands results.

The rhythmic banding process has been observed repeatedly with a number of substances in several different types of jellies. The nature of the jelly is important in certain cases. For example, silver chromate readily forms bands in gelatin but not in agar; and copper chromate readily forms bands in silica jelly whereas silver chromate and lead chromate give bands in this substance only under rather favorable circumstances.[75] It should be emphasized that the presence

[73] Freundlich and Abramson: Z. physik. Chem., **A131**, 278 (1929).

[74] Phot. arch., **37**, 321 (1896); "Chemische Reaktionen in Gallerten," Düsseldorf (1898); Z. anal. Chem., **50**, 82 (1911); Kolloid-Z., **9**, 296 (1911); **12**, 74, 269 (1913); **16**, 76 (1915); Z. physik. Chem., **88**, 1 (1914).

[75] Hatschek: Kolloid-Z., **38**, 151 (1926).

oxidation of a ferrous salt solution with equivalent amounts of sodium iodate and sodium thiosulfate.[62]   Mixtures of α- and γ-monohydrate result from the slow oxidation of ferrous bicarbonate in the air and from the slow oxidation of ferrous chloride at 40–50°, conditions which favor the formation of an intermediate auto-complex.[54]   The pure γ-compound is formed by oxidation of strong solutions of ferrous chloride in the presence of pyridine or of sodium azide in weakly acid solution ($pH = 2.0 - 6.5$).[54]   These observations support Baudisch's[63] view that the formation of γ-monohydrate by the oxidation
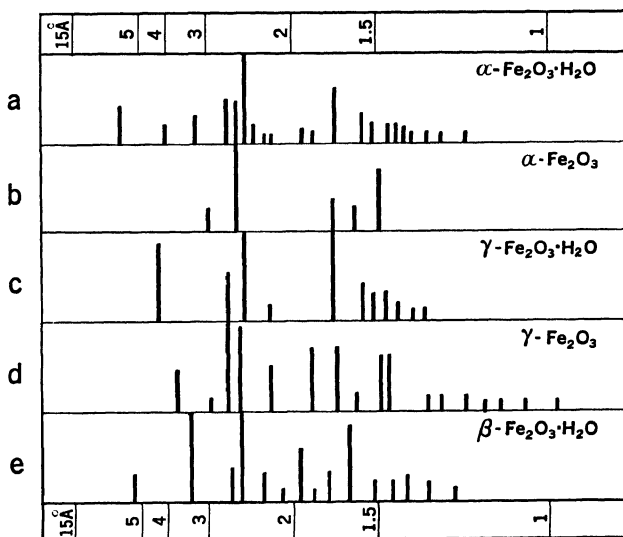
Fig. 6.—Diagrams of the x-ray diffraction patterns of ferric oxides and their hydrates.

of a ferrous salt is preceded by the intermediate formation of an iron complex.   Schikorr[64] likewise suggested that an intermediate green, labile, ferrous-ferric complex is necessary for the formation of γ-$Fe_2O_3 \cdot H_2O$.   Schikorr[65] claimed to get a ferromagnetic monohydrate by oxidation of ferrous hydroxide with hydrogen peroxide; but the possible presence of some ferromagnetic impurity in his preparation has not been excluded.

   [62] Hahn and Hetrich: Ber., **56B**, 1729 (1923); Albrecht: **62B**, 1475 (1929); Albrecht and Wedekind: Z. anorg. Chem., **202**, 205, 209 (1931).
   [63] *Cf.* Krause and Pilawski: Z. anorg. Chem., **197**, 301 (1931).
   [64] Z. anorg. Chem., **191**, 322 (1930).
   [65] Z. anorg. Chem., **212, 33** (1933); *cf.* Quartaroli: Gazz. chim. ital., **63**, 279 (1933)

A diagram of the x-ray diffraction pattern of γ-$Fe_2O_3 \cdot H_2O$ and of the γ-Fe_2O_3 formed by its dehydration are given in Fig. 6 c and d, respectively. Curiously enough, Baudisch and Welo[66] observed that the γ-monohydrate was dehydrated by grinding in a ball-mill giving α-Fe_2O_3 and not γ-Fe_2O_3. Baudisch and Welo[67] have reviewed and discussed the nature and significance of the magnetic properties of γ-$Fe_2O_3 \cdot H_2O$ and of other oxides and oxide hydrates of iron. ·

β-$Fe_2O_3 \cdot H_2O$. Aqueous solutions of ferric chloride when allowed to stand at room temperature or when heated slowly to 60–100°, deposit a yellow hydrous precipitate which is not α-$Fe_2O_3 \cdot H_2O$. Since it contains chloride and gives an x-radiogram differing from α- or γ-Fe_2O_3 or α- or γ-$Fe_2O_3 \cdot H_2O$, it is frequently regarded as a basic ferric chloride.[32] The conditions of formation of the yellow compound are well illustrated by the following experiments:[68] 100-cc portions of freshly prepared ferric chloride solutions were placed in 125-cc flasks supplied with reflux condensers and the rate of heating so regulated that it required 45 minutes for the boiling point to be reached. Continued boiling gave the results summarized in Table II.

TABLE II

HYDROLYSIS OF FERRIC CHLORIDE

FeCl₃ Mols per liter	Color of solution	Color of precipitate (or sol)		
		1 hour	2 hours	3 days
0.01	Yellow	Clear red (sol)	Clear red (sol)	Brick-red
0.02	Yellow	Clear red (sol)	Red (sol)	Brick-red
0.03	Yellow	Clear red (sol)	Reddish yellow (sol)	Brick-red
0.04	Yellow	Clear red (sol)	Yellow (sol)	Brick-red
0.05	Yellow	Yellow	Yellow	Brick-red
0.25	Yellowish brown	Yellow	Yellow	Brick-red
0.50	Reddish brown	Yellow	Yellow	Brick-red
0.75	Reddish brown	Yellow	Yellow	Brick-red
1.00	Reddish brown	Yellow	Yellow	Brick-red

In every case the final product was a brick-red precipitate. In all except the most dilute solutions, a yellow sol or yellow precipitate was

[66] Naturwissenschaften, **21**, 593 (1933).
[67] Chem. Rev., **15**, 1, 45 (1934).
[68] Weiser and Milligan: J. Am. Chem. Soc., **57**, 238 (1935).

obtained as an intermediate product between the solution and the brick-red precipitate. Fifteen years ago, in the absence of x-ray diffraction data, the author concluded that the yellow product formed by slow hydrolysis was a hydrous ferric oxide which differed from the brownish red ferric oxide gel and the brick-red precipitate only in particle size and physical structure (p. 35). It is now known, however, that the aged brown gel and the red precipitate are hydrous hematite, whereas the yellow product is a third polymorphic modification of ferric oxide monohydrate.

The conclusion that the yellow precipitate formed by slow hydrolysis of ferric chloride is ferric oxide rather than a basic salt follows from the observations that the iron : chlorine ratio is not constant but depends on the conditions of formation; and that the chloride content can be reduced to a very low value without in any way altering the x-ray diffraction pattern. The iron : chlorine ratio of the alleged basic salt has been given at various times such values as: 2.33,[69] 4.5,[70] 6.33,[71] 6.67,[72] 7,[73] and 8.[74]   These values are purely accidental, for it has been shown that a certain sample washed once with water and dried at 60° had an iron : chlorine ratio of 4.8; for a similar sample washed with acetone to prevent peptization and dried at 150° the ratio was 6.4; for a third sample dialyzed for 3 weeks and dried at 110° it was 11; for a fourth sample washed with dilute ammonia and dried at 110° it was 28; and for a fifth sample washed more thoroughly with dilute ammonia it was 38. The x-ray diffraction patterns of the five samples were identical in every respect, indicating that the product is ferric oxide containing varying amounts of adsorbed chloride rather than a definite basic salt.

The dehydration isobar for two samples of the yellow oxide in which the iron : chlorine ratio is 38 and 45, respectively, is reproduced in Fig. 7. This shows that the oxide is a monohydrate which loses most of the combined water between 125 and 160°. The temperature of decomposition is higher with samples containing more adsorbed chloride. With the loss of water the color changes from yellow to brick red. X-ray analysis of the red product shows it to be α-Fe_2O_3. A

[69] Wittstein: Chem. Zentr., **15**, 862 (1844).

[70] Ordway: Am. J. Sci. (2) **26**, 197 (1858); Béchamp: Ann. chim. phys. (3) **57**, 296 (1859).

[71] Picton and Linder: J. Chem. Soc., **61**, 157 (1892).

[72] Britton: J. Chem. Soc., **127**, 2148 (1925); Bary: Compt. rend., **187**, 538 (1928).

[73] Bary: Rev. gén. colloïdes, **6**, 209 (1928).

[74] Pickering: J. Chem. Soc., **105**, 472 (1914); Schikorr: Kolloid-Z., **52**, 25 (1930).

similar dehydration takes place by prolonged heating of the yellow monohydrate at 100° under water.

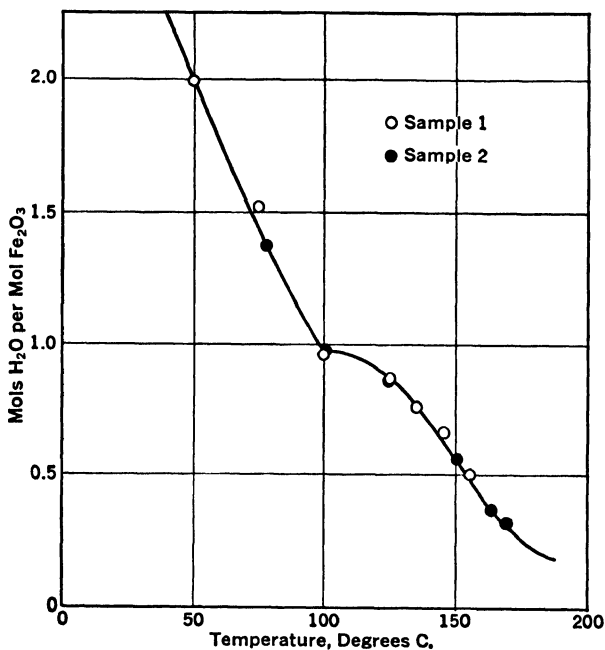A diagram of the x-radiogram of the new monohydrate is given

FIG. 7.—Dehydration isobar of yellow β-ferric oxide monohydrate.

in Fig. 6 e.   It has been named β-ferric oxide monohydrate to distinguish it from the α- and γ-monohydrates.

FERRIC OXIDE SOL

PREPARATION OF POSITIVE SOLS

Positively charged ferric oxide sols are usually prepared by methods which involve either the hydrolysis of ferric salts of univalent anions or peptization of the freshly formed ferric oxide gel.

Hydrolysis Methods

Hydrolysis of Ferric Acetate—Péan de St. Gilles Sol.   Ferric oxide sol was obtained by Péan de St. Gilles[75] by heating a solution of ferric

[75] Compt. rend., **40**, 568, 1243 (1855).

acetate on the water bath for several days. The red-brown color which is characteristic of the acetate becomes brick red as the heating continues, and the peculiar taste of ferric salts gives place to that of acetic acid. The sol is distinctly turbid in reflected light but is clear in transmitted light.

A relatively pure Péan de St. Gilles sol is conveniently prepared by adding just enough acetic acid to a freshly precipitated, thoroughly washed gel of hydrous ferric oxide to carry the gel into solution. In the process some ferric acetate is first formed which peptizes the remaining gel so that much less than the theoretical amount of acetic acid for forming ferric acetate need be used. The resulting mixture is diluted and boiled for several days until the excess acetic acid is removed. The cloudy sol formed in this way is usually described as brick red, but the color varies with the conditions of preparation, a yellow sol being formed if the ferric acetate mixture is allowed to stand for some time at room temperature before subjecting it to the boiling temperature. This is indicated by the observations recorded in Table III.[56] A solution of ferric acetate approximately 3 M with

TABLE III

HYDROLYSIS OF FERRIC ACETATE

Solution boiled		Old solutions		New solutions	
Ferric acetate 0.7 M	Water	Color of sol	Color of precipitate	Color of sol	Color of precipitate
50.0	0.0	Reddish orange	Yellow	Very dark red	Dark red
25.0	25.0	Orange	Yellow	Dark red	Dark red
12.5	37.5	Light orange	Yellow	Red	Dark red
6.3	43.7	Yellow	Yellow	Light red	Dark red
3.2	46.8	Canary	Yellow	Orange-red	Dark red

respect to iron but containing excess ferric oxide was allowed to stand 10 days, after which a 20-cc portion was diluted to 100 cc and from it were prepared 50-cc portions of other solutions of various concentrations, as given in the table. In a similar way, a series of solutions was made up from a freshly prepared solution of ferric acetate. Both sets of solutions were boiled vigorously on an electric hot plate for 15 hours, the water being replaced as it evaporated. A difference in

the color of the two series of sols was soon noted and became quite pronounced as the boiling continued; the colloids from the old ferric acetate were yellow, and from the new, red. After discontinuing the boiling, samples of each sol were precipitated with potassium sulfate and the color of the precipitate noted.

It is now known that the dispersed phase and the precipitate from the red sol were α-Fe_2O_3 whereas that from the yellow sol formed by slow hydrolysis was α-$Fe_2O_3 \cdot H_2O$ (p. 39).

More highly dispersed sols may be obtained by hydrolysis of the acetate if the excess acetic acid is removed by dialysis instead of by prolonged boiling.

Hydrolysis of Ferric Chloride and Nitrate. Probably the most satisfactory method of preparing ferric oxide sol consists in hydrolysis of ferric chloride by pouring a concentrated solution of the salt slowly into boiling water followed by dialysis, preferably in the hot, to remove the hydrochloric acid[76] and thus to avoid reversal of the hydrolytic reaction.[77] Sorum[78] allows 400 cc of a molar solution of pure ferric chloride to flow at the rate of 2 drops per minute into 5 l of boiling water followed by dialysis in the hot. The resulting deep wine-red sol is clear, stable, and almost free from chloride ion. Sols containing no detectable chloride either contain a trace of some other electrolyte or are protected by some material derived from the dialyzing membrane during the prolonged dialysis.

Since ferric chloride hydrolyzes considerably even in the cold, a sol is formed by dialysis of dilute solutions of the salt in the cold.[79] If an attempt is made to heat the solution before the excess ferric chloride is dialyzed out, a yellow sol[80] of β-$Fe_2O_3 \cdot H_2O$ results (p. 42). The yellow β-$Fe_2O_3 \cdot H_2O$ sol is best obtained by thorough washing of the precipitate formed by the slow hydrolysis of a fairly concentrated solution of ferric chloride.[68] If the washing is carried out by the aid of the centrifuge, the chloride content of the gel is reduced to such an extent that a fairly stable but cloudy sol results.

Ferric nitrate[81] may be substituted for ferric chloride in the

[76] Debray: Compt. rend., **68**, 914 (1869); Krecke: J. prakt. Chem. (2) **3**, 286, 295 (1871).

[77] Nichols, Kraemer, and Bailey: J. Phys. Chem., **36**, 505 (1932).

[78] J. Am. Chem. Soc., **50**, 1264 (1928); *cf.* Janek and Jirgensons: Biochem. Z., **180**, 194 (1927).

[79] Van Bemmelen: Z. anorg. Chem., **36**, 382 (1903).

[80] Neidle and Barab: J. Am. Chem. Soc., **39**, 76 (1917); Schikorr: Kolloid-Z., **52**, 25 (1930).

[81] Scheurer-Kestner: Compt. rend., **54**, 616 (1862); Biltz: Ber., **35**, 4433 (1902).

preparation of sols by hydrolysis methods, but its lower hydrolysis constant renders it less satisfactory.[82]

Oxidation Methods

Oxidation of Iron Carbonyl. A sol comparatively free from electrolytes may be obtained by the oxidation of iron carbonyl[83] with hydrogen peroxide, in accord with the following equation:

$$2Fe(CO)_5 + 3H_2O_2 \rightarrow Fe_2O_3 + 10CO + 3H_2O$$
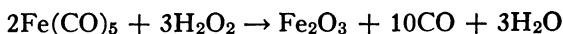
The procedure is as follows: To 800 cc of double-distilled water in a glass stoppered flask are added 5 cc of iron carbonyl and 2 cc of perhydrol. The flask is closed, the contents shaken 5 seconds, and opened to allow the gases to escape. The process is repeated until there is no further reaction. The sol is clear yellow at first, changing to orange and finally to red as the reaction proceeds. The excess iron carbonyl is removed by centrifuging for a few minutes. The sol is coagulated in part by shaking or by bubbling a current of air to remove carbon dioxide. The resulting precipitate can be repeptized by a current of carbon dioxide.

Böhm examined a precipitate from the sol by x-ray diffraction methods and obtained a göthite pattern. For this reason the sol is usually referred to as a göthite sol. But since highly dispersed göthite is yellow and gives a yellow sol it is apparent that the red sol from carbonyl cannot be pure göthite. It probably consists of a mixture of yellow α-$Fe_2O_3 \cdot H_2O$ and of red hydrous Fe_2O_3, the latter being so finely crystalline that its presence is not revealed in the x-radiogram.

Oxidation of Ferrous Salts. Neidle prepared sols by oxidation of ferrous chloride with potassium permanganate[84] or hydrogen peroxide[85] followed by dialysis; and Gavrilov[86] started with ferrous bicarbonate. The best procedure consists in adding 3% H_2O_2 to one equivalent of ferrous chloride dissolved in 2 l of water until all the ferrous ion is oxidized, and purifying the resulting clear, brownish red sol by dialysis either in the hot or the cold. Since sol formation

[82] Neidle: J. Am. Chem. Soc., **39**, 2334 (1917).

[83] Freundlich and Wosnessensky: Kolloid-Z., **33**, 222 (1923); Freundlich and Loebmann: Kolloid-Beihefte, **28**, 392 (1929).

[84] Neidle and Crombie: J. Am. Chem. Soc., **38**, 2607 (1916).

[85] Neidle: J. Am. Chem. Soc., **39**, 2334 (1917); Browne: **45**, 298 (1923).

[86] Kolloid-Z., **37**, 46 (1925).

is the result of hydrolysis following oxidation of the ferrous salt, there is no apparent advantage of the above procedure over one which uses a ferric salt to start. The sol from ferrous bicarbonate differs from the chloride sol in that the former is yellow to brownish yellow whereas the latter is brownish red. The particles of the yellow sol formed at room temperature were probably chiefly $\gamma\text{-}Fe_2O_3 \cdot H_2O$.

Peptization Methods

Addition of a Peptizing Agent—Graham's Sol. Hydrous ferric oxide freshly precipitated from ferric chloride solution with ammonia and thoroughly washed by decantation, preferably by the aid of the centrifuge, is readily peptized by ferric chloride giving a sol that may be purified by dialysis to remove excess ferric chloride and hydrochloric acid. This procedure was first used by Graham,[87] and the resulting sol is frequently referred to as Graham's sol. Unlike the Péan de St. Gilles preparation, Graham's sol is colored deep reddish brown and is clear. Moreover, the coagulum formed by adding electrolytes to a Péan de St. Gilles colloid is granular and difficultly soluble in dilute acids whereas that from a Graham sol is highly gelatinous and is readily soluble in dilute acids.

The peptizing power of ferric chloride is cut down by the presence of alkali chlorides in the order: K < Na < Li; Ba < Sr < Ca < Mg.[88] All this means is that the precipitating action of chloride is less when associated with a strongly adsorbed cation.

Hydrochloric acid may be used instead of ferric chloride as a peptizing agent.[89] It is probable that ferric chloride resulting from interaction of the acid and oxide contributes to the sol-forming process. The weakly dissociated acetic acid and propionic acid are poor peptizing agents compared with hydrochloric acid.[90]

Instead of peptizing the precipitated and washed gel, a sol is frequently prepared by adding to the ferric chloride solution, ammonium carbonate or hydroxide in such an amount that all the precipitate first formed is peptized.[87] The resulting deep brown-red sol is dialyzed to remove ammonium chloride and the excess ferric

[87] J. Chem. Soc., **15**, 249 (1862); Phil. Trans., **151**, 208 (1861).

[88] Dumanskii and Siminova: J. Gen. Chem. (U.S.S.R.) **1**, 1229 (1931); Dumanskii: Kolloid-Z., **60**, 39 (1932).

[89] Müller: Z. anorg. Chem., **57**, 316 (1908); Thomas and Frieden: J. Am. Chem. Soc., **45**, 2523 (1923).

[90] Fair: J. Phys. Chem., **38**, 19 (1934).

chloride. As an example, Neidle and Barab[91] dissolved 25 g of $FeCl_3 \cdot 6H_2O$ in 250 cc of water, added 127 cc of 1.365 N NH_4OH, and after peptization was complete, diluted to 400 cc and dialyzed in the cold to remove the excess ferric chloride, followed by hot dialysis to the desired degree of purity. As already noted, excess ferric chloride must be removed before heating the sol in order to prevent formation of the yellow β-$Fe_2O_3 \cdot H_2O$.

The medicinal preparation "liquor ferri oxychlorati dialysati" is prepared by adding a solution of ammonia (33 parts) to an ice-cold solution of ferric chloride (50 parts). The additions are made in small portions with constant stirring, allowing time between each for the precipitate to be peptized. The resulting clear sol is dialyzed until most of the chloride is removed.[92]

Removal of Agglomerating Electrolytes. Fifty years ago, Wright[93] precipitated a ferric chloride solution with ammonia, evaporated to dryness on the water bath, and washed the residue with water. When most of the chloride was removed,[94] a cloudy red sol ran through the filter paper. This procedure is unsatisfactory for forming a sol since evaporation to dryness causes most of the minute primary particles of the hydrous gel to agglomerate into dense aggregates that are not easily peptized by washing. On the other hand, the general method of washing out the agglomerating electrolytes is readily applicable to the formation of a sol from the freshly precipitated gel. The washing is best accomplished by the aid of the centrifuge or super-centrifuge. The following procedure, which we owe to Bradfield,[31] is particularly useful for preparing a pure sol in the minimum time: Ammonium hydroxide is added to a concentrated solution of ferric chloride with constant stirring until minute floccules of hydrous oxide are barely visible. The more granular precipitate formed by adding an excess of ammonium hydroxide is less reversible. The precipitate is allowed to settle and is washed by decantation until it commences to become colloidal. This solution is then passed through a Sharples Laboratory Supercentrifuge making 32,500 r.p.m., at the rate of 3 l per hour. At the end of the run the sleeve is coated with an extremely finely divided layer of a reddish brown hydrous oxide. This material is removed, mixed to a uniform paste with water, using a mortar and pestle, and is then poured into a large

[91] J. Am. Chem. Soc., **39**, 79 (1917).
[92] "Deutsches Arzneibuch," 400 (1926).
[93] J. Chem. Soc., **43**, 156 (1883).
[94] Kratz: J. Phys. Chem., **16**, 126 (1912).

bulk of water for the next washing. After repeating the process four times, the contents of the bowl can be divided into two distinct parts: (1) a yellowish brown fairly stiff deposit on the lowest 5 cm of the sleeve which grades slowly into (2) a dark red, highly hydrous deposit that is barely stiff enough to adhere to the sleeve. The two fractions are separated, shaken with a small amount of water, and analyzed. From these stock solutions, stable sols of any desired concentration can be prepared. The liquid discharged after the third washing is a beautiful cherry-red sol, containing but a minute trace of chloride.

This procedure has been used repeatedly in the author's laboratory, but in no case was any marked variation observed in the color and physical character of the deposit when a fresh solution of ferric chloride was used. Apparently Bradfield employed an old solution which contained some of the yellow β-$Fe_2O_3 \cdot H_2O$.

Buzágh[95] prepared a brick-red sol of α-Fe_2O_3 by thorough washing of the precipitate obtained by heating the brown gel in an autoclave.

PREPARATION OF NEGATIVE SOLS

Negative ferric oxide may be formed directly under suitable conditions or may result from the reversal of charge on a positive sol.

Direct Precipitation Methods

More than a century ago, Rose[96] observed that glycerol, mannite, sucrose, and glucose will prevent the precipitation of hydrous ferric oxide on adding alkali or ammonia to a solution of ferric salt. This observation was confirmed by Grimaux,[97] who attributed the solubility of the hydrous oxide to the formation of a negative sol stabilized by preferential adsorption of hydroxyl ion.[98] Invert sugar is seven times as effective as cane sugar in preventing the precipitation.[99] In this connection, it is of interest to note that a small amount of hydrous ferric oxide inhibits the crystallization of cane sugar to such an extent that a high percentage of molasses is obtained in plant work if the raw sugar is kept in iron vessels or the clearing "char" contains iron.[100]

[95] Kolloid-Z., 66, 129 (1934).
[96] Ann. chim. phys., 24, 27 (1823).
[97] Compt. rend., 98, 1485 (1884).
[98] Cf. Chatterji and Dhar: Chem. News, 121, 253 (1920).
[99] Riffard: Compt. rend., 77, 1103 (1873).
[100] Thorpe: "Dictionary of Applied Chemistry," 3, 176 (1912).

Robin[101] added ammonia to a mixture containing glycerol, peptone, and ferric chloride. He claimed to get a clear solution of ferric peptonate; but what he had was a negative ferric oxide sol in which both peptone and glycerol functioned as protecting colloids. Fischer[102] used glycerol as a protector in preparing a negative sol to use for intravenous injection in arsenic poisoning. The ordinary positive sol cannot be employed, as it precipitates the negatively charged serum. A negative sol containing excess of both alkali and glycerol does not precipitate serum and is not immediately toxic to rabbits, but it met with limited success in intravenous injections.[43] In this connection, Dozzi[103] reports considerable success in the treatment of anemia by injection of colloidal hydrous ferric oxide.

Powis[104] prepared a stable negative sol without a protecting colloid by allowing 100 cc of 0.01 N FeCl$_3$ to run slowly, with constant shaking, into 150 cc of 0.01 N NaOH. The sol was clear, brownish yellow in color, and showed no sign of precipitation after standing 3 weeks, although a trace of barium chloride caused immediate coagulation.[105]

Grimaux[106] poured an alcoholic solution of ferric ethylate into a large amount of water with vigorous stirring and obtained a sol which Thiessen and Koerner[107] found to be negatively charged and quite instable.

A freshly precipitated ferric oxide gel may be peptized to a negative sol by solutions of alkali salts and acids with multivalent anions that are strongly adsorbed such as sodium arsenate, tartrate, and citrate, and boric, malonic, tartaric, silicic (hydrous SiO$_2$),[108] and molybdic acids.[109]

Methods Based on Reversing Positive Sols

It is frequently possible to reverse the charge on sols by adding an electrolyte with a very strongly adsorbed ion opposite in charge to that on the sol (p. 66). In order to avoid coagulation, the elec-

[101] Compt. rend., **101**, 321 (1885).
[102] Biochem. Z., **27**, 223, 238 (1910); *cf*. Rona and Lipmann: **147**, 172 (1924).
[103] Gazz. ospedali clin., **41**, 182 (1920).
[104] J. Chem. Soc., **107**, 818 (1915).
[105] *Cf*. Keller: Kolloid-Z., **26**, 173 (1920).
[106] Compt. rend., **98**, 105 (1884).
[107] Z. anorg. Chem., **180**, 116 (1929); Vorländer: Ber., **46**, 191 (1913).
[108] Fodor and Reifenberg: Kolloid-Z., **42**, 18 (1927); **45**, 22 (1928).
[109] Dhar and Sen: J. Phys. Chem., **27**, 376 (1923); Sen, Ganguly, and Dhar: **28**, 314 (1924); Dumanskii and Tyazhelova: J. Russ. Phys.-Chem. Soc., **62**, 1313 (1930).

trolyte in excess of the precipitation value must be added all at once with rapid stirring. Among the electrolytes which have been used to make negative sols by charge reversal are sodium hydroxide, [109] disodium phosphate, [110] sodium citrate, [111] and potassium ferrocyanide. [112]

A ferric oxide sol prepared by electrical disintegration of iron electrodes under water is usually positively charged; but it becomes less positive, neutral, and finally negative by repeated filtration through such substances as filter paper, glass wool, cotton, or sand, which are negatively charged in the presence of water. According to Malarski [113] the reversal of charge on the particles is brought about by contact with the negative filtering media. Although this explanation seems plausible, the experiments should be repeated to determine to what extent the properties of the sol are altered by adsorption of stabilizing ions during repeated filtration. Negative sols are formed directly if the disintegration is carried out in a solution of gelatin, which acts as a protecting colloid.

The positively charged sol formed by oxidation of iron carbonyl (p. 47) is reversed by adding a suitable amount of sodium hydroxide. Moreover, the gel which precipitates when the sol is boiled to remove carbonic acid is readily peptized to a negative sol by dilute alkali solution. [83]

CONSTITUTION OF SOLS

Positive Sols

Since the best-known ferric oxide sols are obtained either by peptization of the gel with ferric chloride or hydrochloric acid or by hydrolysis of ferric chloride, the following discussion will be concerned chiefly with sols containing chloride ion.

Water Content. Since the only hydrates of ferric oxide are the yellow α-, β-, and γ-monohydrates, it seems altogether improbable that the red sols of the Péan de St. Gilles type and the Graham type should contain definite hydrates. The characteristic differences between these two types of sols are due neither to chemical structure nor the presence of hydrates, but are the result of differences in the size-distribution curve of the primary colloidal particles. For the

[110] Kruyt and van der Spek: Kolloid-Z., **25**, 18 (1919); Boutaric and Perreau: Compt. rend., **184**, 815 (1927).

[111] Rona and Lipmann: Biochem. Z., **147**, 168 (1924).

[112] Mayanagi: Kolloid-Z., **39**, 321 (1926); Hazel and Ayers: J. Phys. Chem., **35**, 3148 (1931).

[113] Kolloid-Z., **23**, 113 (1918).

Graham type, the maximum lies in the region of exceedingly minute particle size, the position of the maximum shifting toward large particles as we pass to the typical Péan de St. Gilles sol.[114] The conditions under which the sols are formed favor this view. Thus the percentage supersaturation of ferric oxide is much higher for the formation of a typical Graham sol than for the formation of a typical Péan de St. Gilles sol. Differences in the amount of water in different sols are due to differences in specific surface, Graham sols possessing the greater specific surface and, therefore, the larger amount of adsorbed water. If a Graham preparation is impure and dilute, there is a gradual growth and agglomeration of primary particles accompanied by a decrease in the amount of adsorbed water.

The absence of chemical combination between water and ferric oxide in sols prepared by hot dialysis was confirmed by means of freezing-point determinations carried out by Browne.[115] Although the sols contain the oxide in a highly hydrous condition, the effect of dextrose on the freezing point of the sol shows that the water associated with the oxide is adsorbed since all the water in the sol acts as solvent for dextrose or for any other soluble substance.

Whereas the particles in the red sols consist chiefly of the hydrous oxide, those in the yellow sols are hydrous ferric oxide monohydrate. This is true for the yellow Péan de St. Gilles sol which is hydrous α-$Fe_2O_3 \cdot H_2O$ and for the yellow sol obtained by peptization of β-$Fe_2O_3 \cdot H_2O$.

Electrolyte Content. Ferric oxide sols can be prepared fairly free from electrolytes but it has been demonstrated repeatedly that in the absence of protecting colloids some electroltye must be present in the sols to ensure their stability. Thus the common sol formed by hydrolysis of ferric chloride, or by peptization of the hydrous oxide by ferric chloride, always contains traces of chloride, however long the dialysis is continued.[116] A comprehensive study[117] of undialyzed ferric oxide sols formed by boiling dilute solutions of ferric chloride, using ultra-centrifugal, analytical, and light-absorption methods, showed that they contained unchanged ferric chloride, hydrochloric acid, and three principal colloidal fractions: a very highly dispersed, non-centrifugable, semi-colloidal fraction approaching the dispersity of ferric chloride; a major fraction consisting of hydrous ferric oxide particles ranging in

[114] Zsigmondy-Spear: "Chemistry of Colloids," 163 (1917).
[115] J. Am. Chem. Soc., **45**, 297 (1923).
[116] Ufer: "Über kolloides Eisenoxyd," Dissertation, Dresden (1915).
[117] Nichols, Kraemer, and Bailey: J. Phys. Chem., **36**, 326 (1932).

size from 1 to 10 mμ; and a coarser fraction formed by aggregation of the principal fraction.

The presence of chloride in the dialyzed sols led Wyrouboff and Verneuil[118] to suggest that the various preparations contain basic salts or chlorides of "condensed" ferric hydroxides. This idea was further extended and developed by several investigators, especially by Duclaux,[119] Malfitano,[120] and Pauli and his pupils.[124] This general conception of the nature of the sols meets with serious objection at the outset, for Fischer[122] and others[123] have demonstrated that definite chemical oxychlorides of iron do not exist at ordinary temperatures. As a matter of fact, but one basic ferric chloride has been identified, the compound FeOCl prepared by Stirnemann[124] by heating a solution of ferric chloride in a bomb tube between 270 and 410°. Naturally, investigators who assume the existence of definite compounds in ferric oxide sols are unable to agree on their composition. Thus, Nicolardot[125] claims that the sols are made up of mixtures of two compounds in which the ratios of iron to chlorine in equivalents are 6 and 125, respectively. Neidle[82] showed these ratios to be purely accidental but believes there is a compound in which the ratio is 21. Thomas and Frieden[126] conclude that 1 mol of ferric chloride is necessary to keep 21 mols of ferric oxide (ratio of iron to chlorine in equivalents = 42) dispersed in the colloidal condition, irrespective of the concentration of the sol. These observations and conclusions are not in accord with Neidle, who showed that the maximum purity obtainable before precipitation sets in increases appreciably with decreasing iron content. Neidle prepared a sol approximately 0.05 N with respect to iron, in which the ratio equivalents Fe^{+++} : equivalents Cl^- was 84; whereas the maximum purity obtained by Thomas and Frieden at this concentration was only about half as great. Bradfield[31] prepared a ferric oxide sol by centrifugal

[118] Bull. soc. chim. (3) 21, 137 (1899).

[119] J. chim. phys., 5, 29 (1907); 7, 405 (1909); cf. Wintgen: Z. physik. Chem., 103, 250 (1922); Wintgen and Biltz: 107, 403 (1923).

[120] Compt. rend., 148, 1047 (1909); Z. physik. Chem., 68, 236, 248 (1910); Malfitano and Sigaud: J. chim. phys., 24, 104, 184 (1927).

[121] Pauli and Matula: Kolloid-Z., 21, 61 (1917); Pauli and Walter: Kolloid-Beihefte, 17, 256, 319 (1923); Pauli and Valko: Z. physik. Chem., 121, 161 (1926).

[122] Z. anorg. Chem., 66, 38 (1910).

[123] Cameron and Robinson: J. Phys. Chem., 11, 690 (1907); Giolitti: Gazz. chim. ital., 36, 157 (1906); Smith and Giesy: J. Am. Pharm. Assoc., 12, 855 (1923).

[124] Neues Jahrb. Mineral., Geol., A52, 356 (1925).

[125] Ann. chim. phys. (8) 6, 334 (1905).

[126] J. Am. Chem. Soc., 45, 2522 (1923).

washing in which the ratio was 396. In the purest sol Ufer[127] was able to prepare by dialysis, the ratio was approximately 2700.

Fair[90] deduced from the equations for the hydrolysis constant for iron salts of weak acids that the ratio should be constant if the peptizing agents were weak acids. This was found to be approximately true for acids like acetic, butyric, and propionic which have approximately the same peptizing action. With a weak acid like acetic he expected to get a very low ratio, but he got values with an aged oxide of 1.7–4; with a newer oxide he got 9; and Mabee[128] got 20. Fair attributed the larger ratio to the presence of chloride in the sols; but Milligan in the author's laboratory obtained a purity of 18 with a freshly precipitated oxide washed entirely free from chloride with dilute ammonia using the centrifuge.

In the light of the wide variation in the iron : chlorine ratio obtained by different investigators, it is apparent that the composition of a dialyzed colloid depends upon the condition of formation; and that consistent results can be obtained only by a very careful control of the experimental conditions. Since the method of procedure followed by different investigators is likely to vary widely, we might expect the wide variation in the results which the records show. Some people require very little evidence to convince them of the existence of chemical compounds, and they assign definite formulas to the dialyzed sol. Others who have observed the passing of many cherished and time-honored "compounds" content themselves with postulating the formation of a series of "indefinite compounds" in order to explain their observations. This course is of questionable value because of the complexity of the hypothetical compounds that must be assumed to exist.

The idea that the Graham sol contains a basic salt gained support from Böhm's[32] observation that the particles in an aged sol gave an x-radiogram for a basic salt identical with that obtained by the slow hydrolysis of ferric chloride. It will be recalled that the latter precipitate is not a basic salt at all but is β-$Fe_2O_3 \cdot H_2O$ with varying amounts of adsorbed chloride depending on the conditions of formation and the treatment (p. 43). The indefiniteness of composition of the alleged basic salt is recognized by Böhm, who refuses to formulate it; but others, for no reason at all except that Stirnemann made FeOCl as above described, give it the formula of the Stirnemann preparation.

[127] "Über kolloides Eisenoxyd," Dissertation, Dresden (1915); cf. Freundlich: "Kapillarchemie," 511 (1922).
[128] Dissertation, Columbia University (1927).

Malfitano considers the particle to be a complex ion in the Werner sense in which a variable but definite number of $Fe(OH)_3$ molecules are combined with the easily soluble, highly ionized $FeCl_3$ molecules.[129] This may be represented diagrammatically as

$$[Fe(OH)_3]_mFe^{+++}, (Cl^-)_3 \text{ or } ([Fe(OH)_3]_mFeCl)^{++}, (Cl^-)_2$$
$$\text{or } ([Fe(OH)_3]_mFeCl_2)^+, (Cl^-),$$
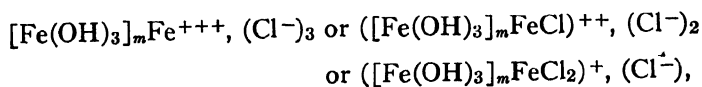
depending on the degree of ionization.

Pauli[130] likewise considers the colloidal particles to be highly complex polyvalent colloidal ions resulting from ionization of complex electrolytes allied to the Werner compounds. Extensive studies were made of sols formed both by peptization and by hydrolysis methods. The chloride content of the sols was determined by direct analysis and by potentiometric methods, and the conductivity was measured at varying dilutions. It was found that not all the chlorine could be detected potentiometrically as chloride ion. The possibility that a part of the chloride was adsorbed[131] either as ion or salt, and so would not be subject to potentiometric measurement, was ruled out, and instead it was assumed that the sol was merely an incompletely dissociated electrolyte which yielded only a fraction of its chlorine as ion.

In support of his theory, Pauli showed that the addition of an electrolyte to the sol which is equally concentrated in chloride ions, causes no displacement of the chloride ion concentration of the sol. Moreover, under certain conditions the cations of an added electrolyte with a common anion may also decrease in concentration, a phenomenon which is attributed to a driving back of the dissociation by the common ion of the ferric oxide sol. As Freundlich[132] points out, neither of these arguments is conclusive. For if the chloride ion is in adsorption equilibrium, as demonstrated by Lottermoser and Maffia, it is only natural that the equilibrium should be maintained if the chloride ion concentration remains unchanged. Furthermore, the fact that the anions in the intermicellar liquid are sufficiently free to drive back the dissociation of an added salt with a common anion

[129] Cf., also, Thomas and Frieden: J. Am. Chem. Soc., **45**, 2528 (1923).

[130] Pauli and Matula: Kolloid-Z., **21**, 49 (1917); Pauli and Rogan: **35**, 131 (1924); Pauli and Walter: Kolloid-Beihefte, **17**, 256 (1923).

[131] Lottermoser and Maffia: Ber., **43**, 3613 (1910); Maffia: Kolloid-Beihefte, **3**, 85 (1911); cf., also, Duclaux: Compt. rend., **143**, 296 (1906).

[132] "Kapillarchemie," 621 (1922).

is likewise in entire accord with the adsorption equilibrium which exists in the sol.[131] Finally, Pauli and Matula[133] emphasize that the behavior of sols as regards conductivity cannot be interpreted simply from the point of view of the dissociation theory. Thus a mixture of ferric oxide sol and alkali chloride, containing equivalent amounts of chloride ion, exhibits a conductivity higher than the arithmetic mean of the conductivity of the components. This is probably due to higher mobility of the colloidal particle owing to an increase in charge by adsorption of a portion of the added cations.

In this connection, Lottermoser[134] found the specific conductance of ferric oxide sols to be higher than that of the ultrafiltrates, the differences being regarded as the true conductivity of the colloidal particles or micelles. If the micelles M are considered to be complex electrolytes, the equivalent conductivity at infinite dilution may be calculated from the equation: $\Delta M_{\infty} = 1000 K_m / K_{Cl}$, where K signifies specific conductance. The mobility of the micelles was found to rise abnormally with purified sols containing but a small amount of chlorine. This fact indicates that the micelles are really adsorption complexes, the abnormality being due to the displacing of the adsorption and hydrolysis equilibria by dilution.

The constitution of the particles of a ferric oxide sol is represented by Pauli as $[x\text{Fe(OH)}_3 \cdot y\text{FeOCl} \cdot \text{FeO}]^+$, (Cl^-), in which $x = 32$ to 350 and $y = 2.16$ to 18 in sols formed by peptization, and $x = 33$ to 130 and $y = 4$ to 5.7 in sols formed by hydrolysis. For example, the electrochemical equivalent, or the "equivalent aggregate" (the amount of colloidal material deposited by one faraday of electricity), of a given sol is estimated to be $[350\text{Fe(OH)}_3 \cdot 18\text{FeOCl} \cdot \text{FeO}]^+$, (Cl^-).

The general point of view of Pauli is accepted by Wintgen,[135] who determines the "equivalent aggregate" of sols from electrical conductivity and transport measurements on the sols themselves and on the ultrafiltrates from the sols. The number of "equivalent aggregates" of sol per liter is termed the normality of the sol, N. From his experimental observations he deduced that in one such sol (containing 1.601 g Fe_2O_3 and 0.06014 g Cl in 100 g of sol) the average composition of the micelles may be represented by the formula:

$$\left(\boxed{75.35\text{Fe}_2\text{O}_3 ; 7.86\text{HCl} ; x\text{H}_2\text{O}}\,\text{FeO}\right)_{10,230}, 10,230\text{Cl}^-.$$
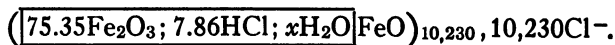
[133] Kolloid-Z., **21**, 49 (1917); cf., also, Mukherjee: Kolloid-Z., **63**, 36 (1933).
[134] Z. Elektrochem., **30**, 391 (1924).
[135] Z. physik. Chem., **103**, 250 (1922); Wintgen and Biltz: **107**, 403 (1923).

Whatever merits Wintgen's formulation of the constitution of colloids may have, it should be pointed out that his work is vitiated by methodical errors (cf. Vol. 1, p. 75). Laing[136] showed that the fraction of the current carried by any charged body whether ion, colloid, wall, or bubble is equal to the ratio of its actual conductivity to the total conductivity of the system. That is:

$$\text{Fraction of current } = c_1 f_1/\mu$$

where c_1 is the concentration and f_1 is the conductivity of unit concentration, and μ is the sum total of all such cf terms for all constituents present. The bodily movement n_1 differs from the above by a factor m which is the number of units to one electrical charge. Thus

$$\text{Bodily movement } = n_1 = c_1 m_1 f_1/\mu$$

McBain[137] points out that Wintgen and his pupils neglected this factor m. They should have divided their mobilities by m_1 to find the conductivity. A further error was made in interpreting U-tube experiments on cataphoresis. Furthermore, McBain and McClatchie[138] showed that the concentration of the ultrafiltrate from a sol varies many-fold with the rate of ultrafiltration, and that it is only with very slow ultrafiltration that the ultrafiltrate approaches the Donnan membrane distribution (cf. Vol. I, p. 315), owing to the presence of charged particles. For example, the pH of a rapidly obtained ultrafiltrate is less than that of the ferric oxide sol, whereas with very slow ultrafiltration it is much greater. In this connection it should be pointed out that accurate determination of the pH value of a ferric oxide sol is impossible with the hydrogen electrode but the glass or quinhydrone electrode works satisfactorily.[139] The failure of Wintgen and others to take these several factors into account makes their estimate of the charge on the colloidal particles much too high.

Fair[90] has given what he calls a new theory of ferric oxide sols. He represents the constitution roughly by the formula

$$[\text{Fe(OH)}_3]_m \cdot x\text{Fe}^{+++} + 3x A^-$$
$$\updownarrow$$
$$\text{Fe}^{+++} + 3\text{OH}^-$$
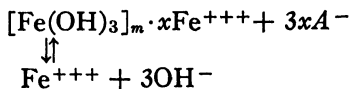
[136] J. Phys. Chem., **28**, 673 (1924).
[137] Colloid Symposium Monograph, **4**, 14 (1926).
[138] J. Am. Chem. Soc., **55**, 1315 (1933).
[139] McClatchie: J. Phys. Chem., **36**, 2087 (1932).

as did Malfitano years before.   This is assumed to hydrolyze progressively to:

$$[Fe(OH)_3]_n \cdot yFe^{+++} + 3yA^- + (x - y)HA$$
$$\Updownarrow$$
$$Fe^{+++} + 3OH^-$$
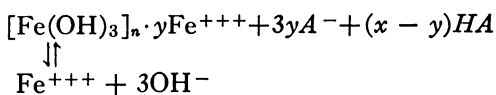
He then derives the mass action equation for the hydrolysis constant in the usual way and of course obtains the usual equations[140] (1) where HA is strong and (2) where HA is weak.   He makes certain deductions from these equations and tacitly concludes that conformity with these deductions is proof of the correctness of the assumptions on which the equations are based.   Unfortunately this is not the case. For, altogether independent of the accuracy of the deductions from the equations, one would arrive at precisely the same equations and therefore could make precisely the same deductions whether one considers the colloidal particle to be a definite chemical individual or to consist fundamentally of hydrous ferric oxide with adsorbed ferric ions which undergo progressive hydrolysis.   Moreover, in the light of what is known of the existence of adsorption forces at surfaces, there seems no justification for assuming the absence of adsorption in a system such as ferric oxide sol where an adsorption equilibrium between extremely minute solid particles of hematite and the surrounding solution must certainly exist.

Summary.   X-ray examination of aged ferric oxide sols free from γ- or β-$Fe_2O_3 \cdot H_2O$ shows that they consist essentially of dispersed hydrous α-Fe_2O_3; and it is probable that, in sols freshly formed in the cold, the dispersed phase is hydrous α-Fe_2O_3 which is too finely crystalline to diffract the x-rays.   In the most common ferric oxide sols the particles are dispersed in a solution containing ferric chloride, hydrochloric acid, and ferric, hydrogen, and chloride ions in varying small amounts depending on the precise method of formation and purification of the sol.   We should therefore expect the hydrous oxide to adsorb these constituents in amounts depending on the physical character of the particles and on the specific adsorbability of the constituents and their concentrations.[141]   Although the particles consist largely of the hydrous oxide they usually contain some chloride which is difficult to displace.   Moreover, the actual composition is determined by the method of formation and subsequent history.   Accordingly, the colloidal particle, exclusive of the outer layer, has a compo-

[140] Denham: J. Chem. Soc., **93**, 41 (1908).
[141] *Cf.* Maffia: Kolloid-Beihefte, **3**, 85 (1911).

sition represented by some point in the three-component diagram: Fe_2O_3-HCl-H_2O, which may be represented symbolically as

$$x Fe_2O_3 \cdot y HCl \cdot z H_2O.$$

It is a well-known fact that a solid substance shows such a strong tendency to adsorb ferric and hydrogen ions, as compared with chlor-
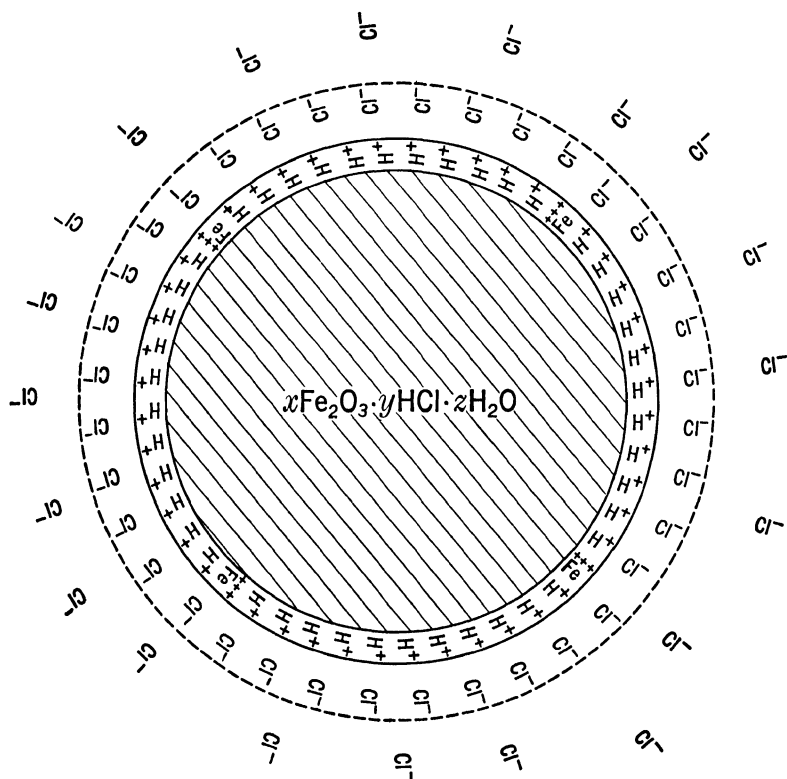
FIG. 8.—Diagrammatic representation of the constitution of a particle of colloidal ferric oxide.

ide, that the particles are surrounded with an ionic double layer with the cations on the inside and chloride on the outside. This is repre-sented diagrammatically in Fig. 8.[142] The inner portion of the double layer consists of adsorbed ferric and hydrogen ions in adsorp-tion equilibrium with the corresponding cations in the intermicellar liquid. The outer portion consists of a diffuse layer of chloride ions,

[142] Weiser: J. Phys. Chem., 35, 1 (1931).

most of which are held by the electrostatic attraction of the adsorbed positive inner layer, but a part of which, because of relatively higher kinetic energy, exert sufficient osmotic repulsive force against the attraction of the double layer to influence the calomel electrode and so may be detected potentiometrically. The latter ions are represented in the diagram beyond the dotted line.

This diagrammatic representation of the structure of the micelle indicates (1) its variability in composition as regards its water and chloride content, (2) the source of its positive charge, and (3) the reason that only a part of the chloride can be detected potentiometrically. If one assumes for the sake of simplicity that the active electrolyte is hydrochloric acid only, the composition may be formulated:

$$[x\mathrm{Fe_2O_3} \cdot y\mathrm{HCl} \cdot z\mathrm{H_2O}]H_n{}^+ \cdot n - q\mathrm{Cl}^-, q\mathrm{Cl}^-$$
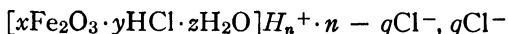
If one prefers to regard ferric oxide sols as electrolytes with colloidal ions it must be emphasized that there is a fundamental difference between sols and non-colloidal complex electrolytes such as potassium ferrocyanide, the cobalt amines, the complex platinic salts, etc., formulated by Werner. There is also a distinct difference between a colloidal ferric oxide and such colloidal electrolytes as the soaps and Congo red in that the latter contain ionic micelles made up of groups of ions which have a definite composition and which carry one charge for each equivalent of the ion, whereas the micelle of the former has no definite composition and may carry hundreds or thousands of equivalents for each free charge.

Negative Sols

Silver chloride sols formed in the presence of a slight excess of silver nitrate are positively charged because the particles adsorb silver ion more strongly than nitrate, whereas silver chloride precipitated with a slight excess of sodium chloride is negatively charged because, in this case, the negative ion is the more strongly adsorbed. Similarly, ferric oxide is positively charged in contact with a small amount of hydrochloric acid because of preferential adsorption of hydrogen ion; and negatively charged in the presence of dilute sodium hydroxide, citrate, or tartrate because of stronger adsorption of the anion than of the cation. Contrary to the behavior of the silver halides, positive ferric oxide sols are much more stable than the negative sols.

Particle Size and Particle Weight

The general methods of determining particle size and particle weight (molecular weight) have been considered in some detail in the first volume of this work, pages 58–71, and will not be repeated here.

Sedimentation Studies. Nichols, Kraemer, and Bailey[143] determined the particle size in ferric oxide sols formed by hydrolysis of dilute ferric chloride solutions, by the sedimentation method, using a low-speed type of ultracentrifuge capable of yielding a maximum

	Time of Hydrolysis	Mean Radius of Particles
I	16 minutes	2.7 mμ
II	60 minutes	2.6 mμ
III	24 Hours	23.0 mμ
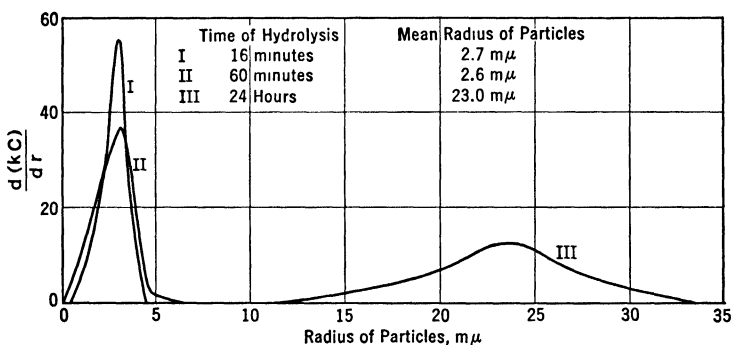
FIG. 9.—Effect of time of hydrolysis of boiling 0.005 N FeCl$_3$ on the "weight optical" distribution curves of colloidal Fe$_2$O$_3$.

centrifugal force of 10,000 times gravity.[144] The particle size is given by the following modification of Stokes' law:[145]

$$r = \sqrt{\frac{9\eta\ln(x + a)/a}{2(d_p - d_m)\omega^2 t}}$$

where r is the radius of the particle in centimeters; η the viscosity of the medium; d_p the density of the particle taken as 4.5; d_m the density of the medium, ω the angular velocity, t the time of centrifuging in seconds; x the distance in centimeters along the cell from the meniscus; and a the distance of the meniscus from the axis of rotation. Some typical observations are reproduced graphically in Fig. 9, which gives the effect of time of hydrolysis on the weight-optical distribution

[143] J. Phys. Chem., **36**, 326, 505 (1932).
[144] Svedberg and Heyroth: J. Am. Chem. Soc., **51**, 550 (1929).
[145] Svedberg and Rinde: J. Am. Chem. Soc., **46**, 2681 (1924).

curves. Since change in concentration is followed optically the term "weight-optical" is introduced to call attention to the fact that an apparent concentration is determined which is the product of the adsorption constant k of the given radius by the concentration C of materials of that radius. Curves were also obtained showing the effect of concentration of ferric chloride on the weight-optical distribution curves. From these observations it was concluded that: (1) at the boiling point, the hydrolytic process is rapid and probably is complete in the first hour; (2) the succeeding digestion favors the secondary process of loss of adsorbed water, development of crystallinity, and growth of crystal size; (3) the secondary aggregation and aging phenomena proceed more rapidly as the concentration of hydrolyzable material is raised. During aging two opposing processes occur: resolution of colloidal particles, especially the smaller ones, and aggregation of the larger particles.

Contrary to the above conclusions, Ayers and Sorum[146] found that the particle size determined by the ultramicroscopic method (Vol. I, p. 58) was independent of the temperature of hydrolysis between 100 and 145° and also independent of the concentration of ferric chloride. The most obvious explanation of this unexpected result is that Ayers and Sorum dialyzed their sols and centrifuged out all the larger particles.

The particle weight or micellar weight was determined from the sedimentation equilibrium by the relation [147]

$$m = \frac{2RT \ln C_2/C_1}{(1 - V\rho)\omega^2 (X_2{}^2 - X_1{}^2)}$$

For spherical particles the particle weight $m = 4/3\pi \cdot r^3 d_p N$, where N is the Avogadro number; R, the gas constant (83.19×10^6); T, the absolute temperature; V, the partial specific volume of the substance; ρ, the density of the solution; C_2 and C_1, the concentrations at the points X_2 and X_1 distant from the axis of rotation of the centrifuge; and ω the angular velocity.

In a sol formed by one hour's boiling of 0.003 M FeCl$_3$, the average value of the particle weight was 300,000 $\pm$ 80,000, and in one formed by boiling 0.005 M FeCl$_3$, the average value was 445,000 $\pm$ 65,000.

Since β-Fe$_2$O$_3 \cdot$H$_2$O formed by slow hydrolysis of ferric chloride goes over to α-Fe$_2$O$_3$ slowly at the boiling point, it is probable that

[146] J. Phys. Chem., **36**, 875 (1930).

[147] Svedberg and Fahraeus: J. Am. Chem. Soc., **48**, 430; Svedberg and Nichols: 3081 (1926); Svedberg: Kolloid-Z., **51**, 10 (1930).

the sols made up from a stock solution of ferric chloride and boiled for only a short time contained some of the β-monohydrate.

Osmotic Behavior. Since a dispersed particle diffuses as a result of the Brownian movement, it follows that a sol should exert an osmotic pressure and freezing-point lowering independent of the electrolyte impurities which must be present to ensure its stability. Duclaux[148] found that the osmotic pressure of a ferric oxide sol increases with the concentration of the sol but is not proportional to it. He demonstrated also that the osmotic pressure falls off slightly with rise in temperature, a result that was confirmed by Zsigmondy.[149] Both Duclaux and Malfitano[150] found that the osmotic pressure does not vary directly with the conductivity, the latter decreasing more.rapidly than the former with dilution of the sol.

The experimental results have been interpreted qualitatively by postulating the presence in the sol of complex basic salts having all the necessary properties; but such an explanation is not very helpful. If we have a suspension that is altogether insoluble and contains no impurities, it will give only a very small osmotic pressure. The osmotic pressure of a Graham sol is due in part to the colloidal particles which have adsorbed ions, but chiefly to the ions of ferric chloride and hydrochloric acid in the intermicellar liquid. Since the behavior of an adsorbed ion will depend on the size and nature of the adsorbing particle, it follows that any factor affecting the physical character of the particles or the adsorption of ions by them will influence the osmotic pressure of the sol. In the nature of things, it is wrong to attribute the observed osmotic pressure and freezing-point lowering of a sol exclusively to the insoluble suspended material, and particle weights deduced on the basis of such an assumption are meaningless.

Optical Properties

Color. The sol of hydrous ferric oxide varies in color from clear brown-red through clear red to cloudy brick red with increasing particle size and decreasing amount of adsorbed water. Pure α- or β-$Fe_2O_3 \cdot H_2O$ sols are yellow; sols intermediate in color between red and yellow are mixtures of hydrous oxide and monohydrate in varying amounts.

[148] Compt. rend., **140**, 1544 (1905); **147**, 131 (1908).
[149] Zsigmondy-Spear: "Chemistry of Colloids," 167 (1917).
[150] Compt. rend., **139**, 1221 (1904); **142**, 1418 (1906).

During the coagulation of clear red Graham sol, the absorption limit moves toward the red at the start but turns back toward the violet again at complete coagulation. This phenomenon has been used to follow the coagulation of the sol photometrically.[151]

Double Refraction. Majorana[152] made the interesting observation that an aged ferric oxide sol exhibits pronounced double refraction when placed in the field of a powerful electromagnet and traversed by a light ray at right angles to the lines of force. This property is undoubtedly due to orientation of the particles of sol by the electric field,[153] since this orientation and the concomitant double refraction can be observed directly by working with a sol containing particles large enough to see with an ordinary microscope. Moreover, a gel formed by coagulation of a sol in an electric field exhibits permanent double refraction, whereas coagulation under ordinary conditions gives an optically inactive gel. Large particles cause a greater effect than small ultramicrons since the Brownian movement of the ultramicrons prevents sufficient orientation to cause pronounced double refraction. Cotton and Mouton attribute the optical phenomenon to the particles themselves and not to their position alone.[154] This is in accord with Freundlich's[155] observation that colloidal solutions of ferric oxide and vanadium pentoxide (p. 291), showing the Majorana phenomenon, exhibit double refraction when stirred mechanically[156] or when a current of electricity is passed through the sols. These observations support the view held by Nägeli[157] a long time ago, that the particles of certain sols consist of anisotropic ultramicrons having a resemblance to tiny crystals.

Viscosity

The viscosity of hydrous oxide sols generally increases with increasing concentration of sol. A freshly formed sol has a higher viscosity

[151] Jirgensons: Kolloid-Z., **44**, 203 (1928); Boutaric: Bull. sci. acad. roy. Belg. (5) **10**, 560 (1924); Hildebrand and Sorum: J. Phys. Chem., **38**, 809 (1934).

[152] Atti accad. Lincei (5) **11** (I), 374, 463, 531; **11** (II), 90, 139 (1902).

[153] Schmauss: Ann. Physik (4) **12**, 186 (1903); Cotton and Mouton: Compt. rend., **141**, 317, 349 (1905); Ann. chim. phys. (8) **11**, 181 (1907).

[154] Heller and Zocher: Z. physik. Chem., **A166**, 365 (1933); Heller: Kolloid-Beihefte, **39**, 1 (1934).

[155] Z. Elektrochem., **22**, 27 (1916); Diesselhörst and Freundlich: Physik. Z., **16**, 422 (1915); **17**, 125 (1916).

[156] *Cf.* Quincke: Ann. Physik (4) **15**, 28 (1904); Tieri: Atti accad. Lincei (5) **19** (I), 470 (1910).

[157] "Theorie der Gärung," München, 121 (1879).

than an aged one,[158] and the higher the temperature of formation
the lower the viscosity.[159]   Since prolonged standing and high
temperature favor the loss of adsorbed water by the particles and
decrease its stability toward electrolytes, it seems altogether likely
that there is a direct connection among the decrease in the hydrous
character of the particles, the decreased viscosity, and the lowered
stability.[159]

The stepwise addition of salt solutions to ferric oxide sols causes
a slight falling off in the viscosity followed by a marked increase.[160]
The cause of the initial decrease is not obvious but it is probably
associated in some way with a slight peptization of secondary aggre-
gates or with a reduction in the hydration of the particles.   The sub-
sequent decrease in viscosity is due to agglomeration of the particles
into a kind of network that offers resistance to flow.   With sufficiently
concentrated sols this agglomeration may result in jelly formation
(p. 84).   Increasing the pH value of a sol causes but little change in
viscosity until about $pH = 7$, when it mounts rapidly, probably
because of agglomeration.

Electrical Properties

Cataphoresis.   Some typical data on the migration of colloidal
particles of ferric oxide in an electric field have been obtained by
Hazel and Ayers,[161] using a cell for ultramicroscopic observations
designed by Mattson.[162]   For a given sol the velocity at unit poten-
tial gradient is determined by the charge on the particles.   Since the
positive charge is due to preferential adsorption of hydrogen ions,
a gradual increase in the pH value first lowers the charge and hence
the mobility to zero at a pH of approximately 8.6.   Above this value
the charge is reversed and the mobility of the resulting negatively
charged particles increases with increasing pH value, owing to increased
adsorption of hydroxyl ion.   The observations of Hazel and Ayers
for a sol containing 0.006 g Fe_2O_3 per l are shown graphically in

[158] Pauli and Matula: Kolloid-Z., **21**, 58 (1917); Dhar and Chakravarti: **42**, 121
(1927); Z. anorg. Chem., **168**, 210 (1928).

[159] Ayers and Sorum: J. Phys. Chem., **34**, 2826 (1930).

[160] Woudstra: Kolloid-Z., **8**, 73 (1911); Dhar and Chakravarti: **42**, 124 (1927);
Yoe and Freyer: J. Phys. Chem., **30**, 1389 (1926).

[161] J. Phys. Chem., **35**, 2931, 3148 (1931); Hazel and McQueen: **37**, 553, 571
(1933); cf. Mukherjee, Roychoudhury, and Palit: J. Indian Chem. Soc., **10**, 713
(1933); Pauli and Neurath: Kolloid-Z., **70**, 135 (1935).

[162] J. Phys. Chem., **32**, 1532 (1928).

Fig. 10, in which the velocity of the particles under unit potential gradient is plotted against the pH value.
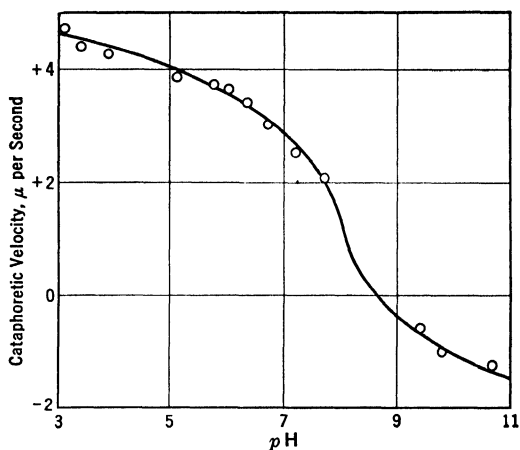
FIG. 10.—Effect of the pH value of ferric oxide sol on the cataphoretic velocity of the particles.
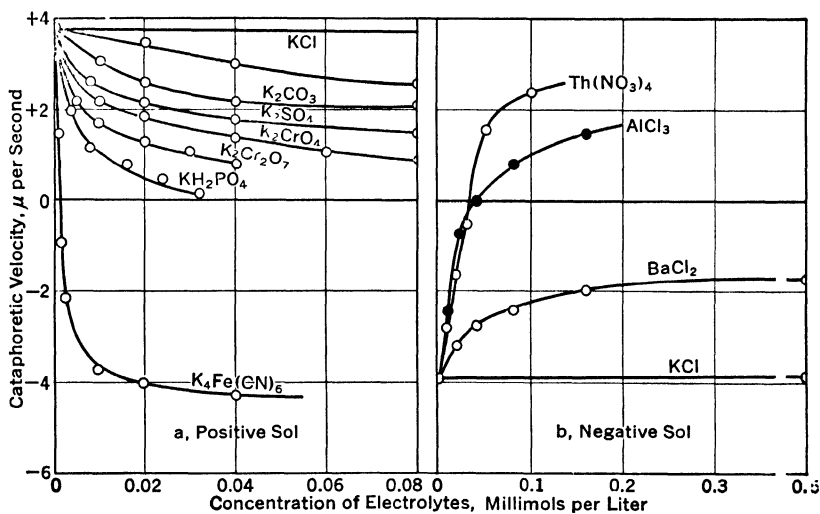
FIG. 11.—Effect of electrolytes on the cataphoretic velocity of the particles in ferric oxide sols.

The addition of salts likewise lowers the charge on the positive sol; but charge reversal takes place only in the presence of very strongly adsorbed multivalent anions such as ferrocyanide. Some

typical observations on the above-mentioned sol are shown graphically in Fig. 11a. Desai and Barve[163] observed an initial increase in velocity followed by a decrease with potassium chloride and magnesium chloride but not with potassium sulfate. For the positive sol the anion is the effective ion, the lowering at a given concentration being in the order:

$$Cl < CO_3 < SO_4 < CrO_4 < Cr_2O_7 < H_2PO_4 < Fe(CN)_6^{IV}.$$

The significance of this in connection with the coagulation of sols will be considered in the next section.

It will be noted that the action of the ferrocyanide ion is so marked that, even at quite low concentrations, it reverses the charge on the particles, giving a negative sol. Some migration data on the negative sol formed in this way are shown in Fig. 11b. Here the cations are effective in lowering the charge, the order being: $K < Ba < Al < Th$. At concentrations less than 1 millimol per liter the strongly adsorbed multivalent aluminum and thorium ions reverse the charge, re-forming positive sols.

It is a common procedure to calculate the so-called ζ-potential of the double layer at the surface of the particles assumed to be spheres, from the mobility u of the particles, by the expression:[164]

$$\zeta = \frac{6\pi\eta u}{HD}$$

where H is the potential gradient in volts per centimeter and D and η are the dielectric constant and viscosity, respectively, of the medium. This is of questionable value since McBain[165] points out that the equation is altogether inadequate for calculating the ζ-potential. It appears wiser to use the u-value which gives a direct quantitative expression of all electrokinetic phenomena rather than to use an erroneous, if not fictitious, ζ-potential. Lottermoser and Chang[166] showed that the ζ-potential of colloidal particles calculated by the above equation does not change if a portion of the sol is diluted with the ultrafiltrate from the sol; but the ζ-potential falls off if the sol is diluted with water.

Conductivity. Since the particles in a sol move in an electric field,

[163] Nature, **128**, 907 (1931); cf., also, Desai and Borkar: Trans. Faraday Soc., **29**, 1269 (1933).

[164] Debye and Hückel: Physik. Z., **25**, 49 (1924).

[165] J. Indian Chem. Soc. (Ray Commemoration Vol.) 67 (1933); cf., however, Audubert: J. chim. phys., **30**, 89 (1933).

[166] Kolloid-Z., **64**, 268; **65**, 62 (1933).

a sol will possess a conductivity independent of the presence of electrolytes. In a metallic sol such as gold, most of the conductivity appears to be due to electrolyte impurities in the dispersion medium (Vol. I, p. 76). This is not the case in certain ferric oxide sols. For example, McBain and McClatchie[138] prepared a sol containing 0.912 gram equivalent of iron and 0.044 gram equivalent of chlorine by adding ammonia to 0.9 M FeCl₃ short of precipitation and dialyzing in the cold for 2 months. The specific conductivity of the sol was found to be 5.70×10^{-4}, of which 5.40×10^{-4} was due to the colloidal particles and their oppositely charged chloride ions. As already pointed out (p. 58), the composition of the ultrafiltrate from a sol varies with the rate of ultrafiltration, the most rapid rates yielding the lowest concentrations of ultrafiltrate, and a form of dialysis the highest. Failure to take this factor into account invalidates the estimate of the composition of the colloidal particle obtained by Wintgen and others, from conductivity and transport data.

Catalytic Action

Colloidal ferric oxide catalyzes the decomposition of hydrogen peroxide (Vol. I, p. 239). The phenomenon was investigated by Kepfer and Walton[167] using a chloride-free, Sorum sol at 50°. The reaction appeared to be monomolecular, but the velocity constant increased as the reaction progressed. The temperature coefficient of the reaction velocity between 30 and 60° was 2.33 for each rise of 10°, indicating that the rate of decomposition was governed by a chemical change and not by the rate of diffusion. The addition of such electrolytes as sodium and barium chloride influences the process by adsorption and agglomeration which alter the extent of the catalytic surface; this influence is modified with such electrolytes as primary and secondary sodium phosphate, hydrochloric acid, sodium hydroxide, and copper sulfate, by the specific effect of the electrolyte on the stability of the solution of hydrogen peroxide.

The catalytic activity of the sol decreases with age owning to increase in particle size with consequent decrease in specific surface.[168]

<center>COAGULATION OF FERRIC OXIDE SOLS</center>

Coagulation by Electrolytes

Precipitation Values. The precipitating power of a few electrolytes for two different positive sols and one negative ferric oxide sol

[167] J. Phys. Chem., **35**, 557 (1931).

[168] Teletov and Alekseeva: Ukrain. Khem. Zhur., **6**, Sci. Part, 61 (1931).

is shown by the observations of Freundlich[169] collected in Table IV. These data are typical of what one encounters in electrolyte coagulation. The anions are most effective in precipitating negative sols

TABLE IV

PRECIPITATING VALUES OF ELECTROLYTES FOR FERRIC OXIDE SOLS
(Millimols per liter)

Positive Graham sol 0.823 g Fe_2O_3/l		Positive sol from $Fe(CO)_5$ 0.46 g Fe_2O_3/l		Negative sol from $Fe(CO)_5$ 0.46 g Fe_2O_3/l	
NaCl	9.25	KI	8.4		
KCl	9.00	KCl	5.4	KCl	22.0
$\frac{1}{2}BaCl_2$	9.65	KCNS	2.7	$CaCl_2$	0.07
KBr	12.5	$\frac{1}{2}BaCl_2$	6.4	$BaCl_2$	0.09
KI	16.0	$\frac{1}{3}AlCl_3$	>200.0	$AlCl_3$	6.4
KNO_3	12.0	$\frac{1}{3}La(NO_3)_3$	45.0	$La(NO_3)_3$	0.7
$\frac{1}{2}Ba(NO_3)_2$	14.0	Sodium			
K_2SO_4	0.205	salicylate	0.26		
$MgSO_4$	0.22	Strychnine		Strychnine	
Tl_2SO_4	0.22	nitrate	4.8	nitrate	4.0
$K_2Cr_2O_7$	0.195	K_2SO_4	0.082		

and the cations in precipitating positive sols; but the ion having the same charge as the sol cannot be neglected. Thus the precipitation value of barium chloride is higher than that of potassium chloride for a positive sol because of the stabilizing effect of the divalent barium ion. The precipitation values of electrolytes with divalent precipitating ions are much greater than those with univalent precipitating ions. This is further illustrated by Freundlich and Zev's[170] observation that the precipitating power of complex cyanides for ferric oxide sol is in the order:

$$Fe(CN)_6^{IV} > Fe(CN)_6^{III} > (CN)^{II} > Au(CN)_2^{I}.$$
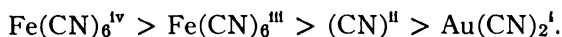
With ions of the same valence in an homologous series, the coagulation power increases with the molecular weight of the anion.[171]

[169] Z. physik. Chem., **44**, 151 (1903); Freundlich and Wosnessensky: Kolloid-Z., **33**, 225 (1923).
    [170] Z. physik. Chem., **114**, 81 (1925).
    [171] Freundlich and Birstein: Kolloid-Beihefte, **22**, 99 (1926); Freundlich and Slottman: Z. physik. Chem., **129**, 316 (1927).

The precipitation value decreases with decreasing concentration of sol as shown by observations[172] on a Péan de St. Gilles ferric oxide sol given in Table V and reproduced graphically in Fig. 12. The

TABLE V

PRECIPITATION OF FERRIC OXIDE SOLS

Concentration of colloid, %	Precipitation values of		
	KBrO$_3$	K$_2$SO$_4$	K$_4$Fe(CN)$_6$
100 (1.7 g per l)	40.1	0.68	0.57
50	34.4	0.41	0.30
25	28.0	0.25	0.16
12.5	25.0	0.16	0.08

falling off of the precipitation value with dilution is approximately proportional to the change in concentration of sol for salts with multivalent precipitating ions,[173] but is much less for salts with univalent precipitating ions. Indeed, the precipitation value of potassium chloride actually increases with dilution of negative arsenic trisulfide sol[174] and even of very highly purified ferric oxide sol.[175]
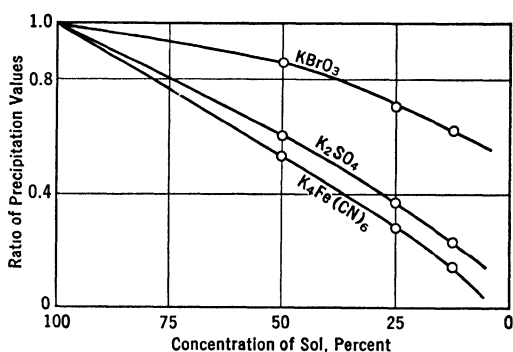
FIG. 12.—Effect of concentration of ferric oxide sol on the precipitation values of electrolytes.

Three factors determine the effect of dilution of sol on the precipitation value of electrolytes: (1) the smaller number of particles in the weaker sol requires less electrolyte to lower the ζ-potential to the agglomeration point; (2) the decreased chance of collision in the diluted sol requires a lower potential and hence more electrolyte to

[172] Weiser and Nicholas: J. Phys. Chem., **25**, 742 (1921).

[173] Takamatsu: Kolloid-Z., **38**, 229 (1926).

[174] Burton and Bishop: J. Phys. Chem., **24**, 701 (1920).

[175] Sorum: Kolloid-Z., **58**, 314 (1932); *cf.* J. Phys. Chem., **39**, 283 (1935).

cause coagulation in a given time;[176] (3) the stabilizing effect of the ion having the same charge as the sol.[172] Of these three factors (1) is most important with electrolytes containing strongly adsorbed multivalent precipitating ions that require but low concentrations; (2) can usually be disregarded, whereas (3) is of primary importance if the precipitation value is quite high, as it generally is with uni-univalent electrolytes.

The rates of slow coagulation of highly purified sols have been measured by Hildebrand and Sorum[177] by observing the effects of the transmitted light on a photoelectric cell after the addition of different concentrations of sodium salts. No induction period was noted in any case, and the process was not autocatalytic (pp. 119 and 274). Apparently the flocculation process is autocatalytic only if the sols are relatively impure.

Adsorption of Precipitating Ions—Acclimatization. During the coagulation of positively charged ferric oxide sol, the anions of the precipitating electrolyte are carried down by the coagulum. For a Péan de St. Gilles sol the order of adsorption[178] is: phosphate > citrate > tartrate > oxalate > sulfate > iodate. The amounts of the several ions adsorbed do not represent the amounts required to lower the potential on the particles to the point of agglomeration but are considerably larger, since adsorption by the agglomerating particles takes place. The adsorption values are not equivalent for the various types of ions even of the same valence. Salts of sodium and potassium have little effect on the adsorption of cupric ions by the oxide, but ammonium salts cut down the adsorption appreciably.[179] The effect of the hydrogen ion concentration on adsorption during coagulation of hydrous oxide sols will be considered in a later chapter (p. 142).

Since adsorption by neutralized colloidal particles during agglomeration is never negligible and may rise to large proportions, it is not surprising that such colloids as hydrous ferric oxide,[180] arsenic trisulfide,[180] and albumin[181] require less electrolyte to cause precipitation when added all at once than when added stepwise through a long interval of time, particularly when the slow addition produces

[176] Kruyt and van der Spek: Kolloid-Z., **25**, 3 (1919).

[177] Hildebrand and Sorum: J. Phys. Chem., **38**, 809 (1934).

[178] Weiser and Middleton: J. Phys. Chem., **24**, 53, 72 (1920).

[179] Hamence: Trans. Faraday Soc., **30**, 299 (1934).

[180] Freundlich: Z. physik. Chem., **44**, 143 (1903); Dumanskii and Solin: Kolloid-Z., **59**, 314 (1932).

[181] Höber and Gordon: Beitr. chem. Physiol. Path., **5**, 436 (1904).

fractional precipitation of the sol. This phenomenon is known as "acclimatization," the connotation being that the colloid becomes acclimatized to its surrounding when the electrolyte is added slowly, and so more is required to produce a given result. It would appear, however, that the necessity for using more electrolyte to effect complete precipitation on slow addition arises not so much from the adaptability of the colloid to the presence of electrolytes, as from fractional precipitation which not only removes ions owing to adsorption by neutralized particles but also alters the stability of the sol by decreasing its concentration. From this point of view, the factors which determine the excess required for a given slow rate of addition are: the extent to which the colloid undergoes fractional precipitation; the adsorbing power of the precipitated colloid; the adsorption of the precipitating ions; and the effect of dilution of the sol on the precipitation concentration of electrolytes.[182]

Displacement of Chloride; Titration of So!s. In the coagulation of sols formed from ferric chloride the precipitating anion is taken up by the particles in exchange with chloride.[183] Rabinovich and Kargin [184] followed the change in the chloride ion concentration potentiometrically on adding sulfate and other ions stepwise to a definite amount of sol. Erroneous conclusions were drawn from the observations because too little time was allowed for equilibrium to be established.[185] The procedure used in the author's laboratory was as follows: Pure, freshly precipitated calomel was suspended in the aged ferric oxide sol. A 20-cc portion of the sol was placed in the outer compartment of a glass mixing apparatus and a definite amount of electrolyte diluted to 5 cc in the inner compartment. After mixing, the mixture was transferred to a small bottle which was kept in the thermostat at 25° for 2 days, shaking at intervals to saturate with calomel. The mixture was then placed in an electrode vessel consisting of a 30-cc weighing bottle in the bottom of which was sealed a platinum wire making contact with mercury in the bottom of the vessel. After 24 hours the potential of the resulting half-element was measured against a standard calomel electrode. A series of such half-elements was made with the amount of electrolyte increasing

[182] *Cf.* Weiser: J. Phys. Chem., **25**, 413 (1921); **30**, 20 (1926).

[183] Pauli and Matula: Kolloid-Z., **21**, 54 (1917); Pauli and Rogan: **35**, 133 (1924); Pauli and Walter: Kolloid-Beihefte, **17**, 256 (1923).

[184] Z. physik. Chem., **A133**, 203 (1928); Rabinovich and Fodiman: **A159**, 403 (1932).

[185] Weiser and Gray: J. Phys. Chem., **36**, 2178 (1932).

stepwise. A typical set of observations is shown in Table VI and represented graphically in Fig. 13. Similar observations with several electrolytes are summarized in Fig. 14.
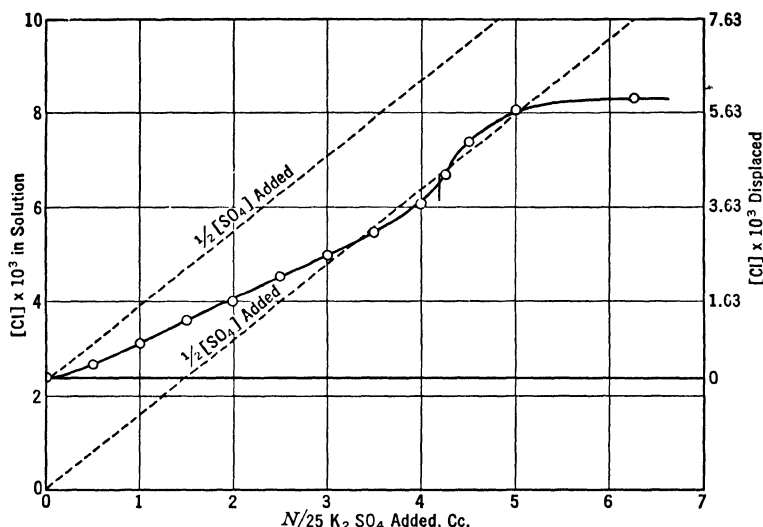
FIG. 13.—Titration curve of ferric oxide sol with potassium sulfate.
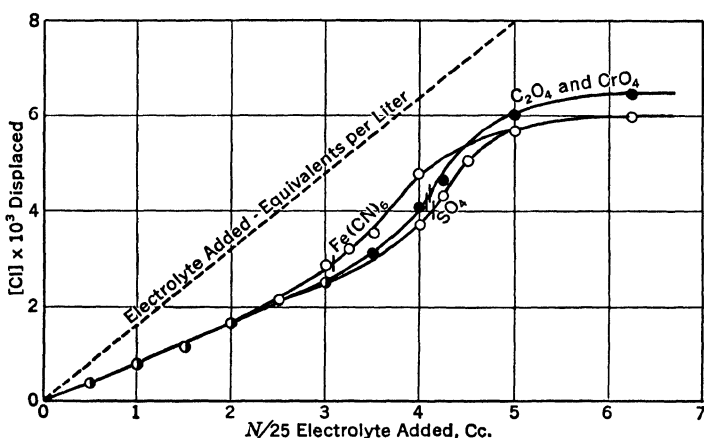
FIG. 14.—Titration curves of ferric oxide sol with several electrolytes.

These and other observations of phenomena which take place during the coagulation of ferric oxide sol may be summarized as follows: [142] (1) At the precipitation value of potassium salts of mul-

TABLE VI

TITRATION OF Fe_2O_3 SOL II WITH K_2SO_4

Cc of K_2SO_4 added to 20 cc of Sol Total volume 25 cc	π volts	αCl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	[Cl] equivalent to [SO$_4$] added $\times 10^3$
0.0	0.0910	2.29	2.37	0.0	0.0
0.5	0.0880	2.58	2.69	0.32	0.80
1.0	0.0843	2.98	3.11	0.74	1.60
1.5	0.0804	3.48	3.64	1.27	2.40
2.0	0.0778	3.83	4.02	1.65	3.20
2.5	0.0748	4.31	4.54	2.17	4.00
3.0	0.0727	4.67	4.93	2.56	4.80
3.5	0.0700	5.19	5.49	3.12	5.60
4.0	0.0675	5.73	6.07	3.70	6.40
4.25	0.0647	6.38	6.68	4.31	6.80
4.50	0.0626	6.93	7.40	5.03	7.20
5.00	0.0605	7.52	8.04	5.67	8.00
6.25	0.0597	7.76	8.31	5.94	10.00

tivalent ions the chloride in the supernatant solution is equivalent to or but little greater than the amount of added electrolyte. (2) Only a part of the chloride that is found in the supernatant solutions, after precipitation, can be detected potentiometrically in the original sol before adding electrolyte. Not all the chloride in the micelles is displaced by a large excess of precipitating electrolyte. (3) The chloride measured potentiometrically, following the stepwise addition of electrolyte, consists of the chloride in the sol originally, together with an additional amount that is displaced when the added anion is taken up. (4) The multivalent ions investigated are taken up practically completely by the sol particles in concentrations up to and including the precipitation concentration. The chloride displaced so that it can be detected potentiometrically is less than half the amount equivalent to the multivalent ion taken up. (5) The amount of chloride displaced follows nearly a linear course at the outset of the stepwise addition of multivalent ions but becomes proportionately greater as the precipitation concentration is approached. (6) The chloride displacement curves for multivalent ions of varying valence follow an almost identical course until the precipitation concentration is approached, when a marked divergence for ions of different valence is observed. (7) The three salts of divalent anions exhibit a strik-

ingly similar behavior as regards the entire course of the chloride dis-
placement curves and the precipitating power. (8) The trivalent
ferricyanide coagulates at a distinctly lower concentration than the
divalent ions, and the chloride displaced at the precipitation value is
proportionately less with the former than with the latter. (9) The
chloride displacement curve with potassium salts of univalent ions,
such as nitrate, follows a course distinctly lower than that for the
multivalent ions.

Mechanism of the Coagulation Process. Two general theories of
the mechanism of the coagulation process have been proposed: the
adsorption theory and what may be termed the solubility theory. It is
obvious that any satisfactory mechanism must explain the facts noted
in the preceding paragraph.

The Adsorption Theory. The adsorption theory assumes that
coagulation takes place as a result of lowering of the ζ-potential on the
particles by adsorption of the ion of the electrolyte opposite in charge
to that on the sol. If the constitution of the sol particle is represented
diagrammatically as in Fig. 15 a (*cf*. p. 60), the adsorption mechanism
of the process may be represented in the following way: On adding
an electrolyte such as potassium sulfate to the sol, the divalent sulfate
being more strongly adsorbed than chloride forces itself into the
double layer closer to the adsorbed hydrogen and ferric ions and dis-
places chloride as indicated diagrammatically in Fig. 15 b. Potenti-
ometric analysis enables one to determine the chloride which has been
displaced. The difference between the chloride in the sol originally
and that after the addition of sulfate, in other words, the displaced
chloride is not equivalent to the adsorbed sulfate since a part of the
sulfate which enters the layer corresponds to chloride measurable
potentiometrically in the original sol.

The adsorbed sulfate lowers the potential on the particle in the fol-
lowing way: A sulfate ion has the same average kinetic energy as a
chloride ion but it possesses double the charge. Accordingly, if one
assumes for the moment that the valence only determines the adsorba-
bility, the divalent particles in the outer layer would be drawn close
to the inner layer and the thickness of the double layer would be
decreased. Since the potential difference between two layers of
opposite sign with constant charge density is directly proportional to
the distance between them, it follows that the reduced thickness
of the layer will be accompanied by a decrease in potential on the
particle.

Since the three divalent ions: sulfate, oxalate, and chromate,

exhibit such a strikingly similar behavior in displacing chloride and in reducing the charge to the coagulation value, it follows that with these three ions the valence is the most important factor determining the adsorbability.

The behavior of trivalent ions such as ferricyanide would follow from what has been said. The ions having the same average kinetic energy but with three charges will be drawn closer to the inner layer
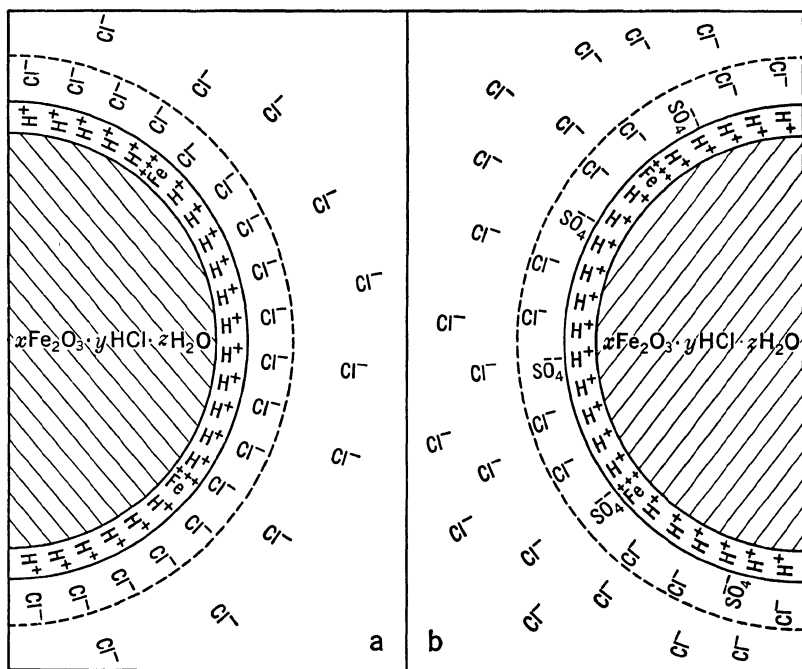
FIG. 15.—Diagrammatic representation of the constitution of a particle of colloidal ferric oxide before and after the addition of potassium sulfate.

than the divalent ions, and the further reduction in thickness of the double layer manifests itself in a lower precipitation value. The chloride ion displaced is obviously less, since less ferricyanide needs to be adsorbed to lower the charge on the particles to the coagulation value.

The adsorption of both the divalent and trivalent ions is sufficiently great that the amount necessary to cause coagulation is practically completely adsorbed. The adsorption at this concentration is not

completely irreversible, however, since shaking the precipitated gel with water results in partial repeptization of the sol owing to the breaking away of some of the precipitating ions from the close adsorption layer.

The increase in the chloride displaced for a given increment in the multivalent ion added in the region of the precipitation value is the result of agglomeration and partial coalescence of the colloidal particles into micelles having a lower specific surface for a given mass.

The behavior of nitrate ion as compared with multivalent ions might be inferred from what has gone before. A much higher concentration of the univalent ions is necessary to produce the same effect as the multivalent ions since the latter are attracted so much more strongly toward the adsorbed hydrogen ion and so would be expected to effect the necessary lowering of potential in much lower concentration. The smaller amount of chloride displaced by nitrate as compared with the multivalent ions is not surprising in view of the fact that chloride is quite as effective as nitrate in lowering the potential. Some chloride is displaced because the higher concentration of nitrate causes some of it to enter the double layer and force out an equivalent amount of chloride.

The Solubility Theory. Duclaux[186] determined the precipitation values of sodium sulfate, citrate, chromate, carbonate, phosphate, hydroxide, and ferrocyanide for a Graham sol containing 203×10^{-3} equivalent of iron and 16.6×10^{-3} equivalent of chlorine per l, and found them to vary from 13×10^{-3} equivalent per l in the case of ferrocyanide to 19×10^{-3} in the case of phosphate. These observations were believed to show that equivalent amounts of the various anions cause the same effect, and furthermore, that the amount necessary for precipitation is the same as the chloride content of the sol within the limits of experimental error. A marked variation from the equivalence rule was observed with sodium chloride and sodium nitrate which required 2000×10^{-3} and 1880×10^{-3} equivalent per l, respectively, to precipitate the same amount of sol as the seven salts mentioned above.[187] Impressed by the similarity in the precipitating power of multivalent ions, Duclaux came to regard the precipitation process as a definite stoichiometric chemical reaction, a double decomposition of the ordinary type with the formation of an insoluble salt. A similar view is held by Nicolardot,[188] Pauli,[183]

[186] J. chim. phys., **5**, 36 (1907).
[187] *Cf.* Boutaric and Bouchard: Compt. rend., **191**, 613 (1930).
[188] Ann. chim. phys. (8) **6**, 362 (1905).

and Fair.[90] Thus Pauli formulates the alleged reaction with potassium sulfate as follows:

$$2[xFe(OH)_3 \cdot yFeOCl \cdot FeO]Cl + K_2SO_4$$

$$= [xFe(OH)_3 \cdot yFeOCl \cdot FeO]_2SO_4 + 2KCl$$
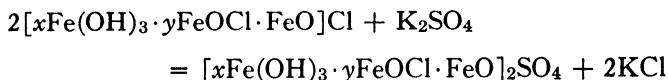
Actually, of course, the alleged insoluble sulfate is not thrown down until a critical concentration of sulfate is added. This anomalous behavior as compared with that in the precipitation of simple insoluble compounds calls for an explanation. "The addition of sulfate and similarly acting salts to the sol," say Pauli and Walter,[189] "causes precipitation owing to the formation of insoluble compounds. The anomalous behavior as compared to simple electrolytes, namely that an amount of sulfate almost equivalent to the entire chlorine content of the sol is necessary for flocculation, is explained by a peculiar equilibrium between the complex bound and the ionic chlorine as well as by the peptizing action of the undischarged complex. The coagulated sol has the formula of a complex double salt, a chlorine-poor and sulfate-rich chlor-sulfate. The ratio of chlorine to sulfate is in the first instance a function of particle size. It increases with particle size since the analytically determined maximum exchange of chlorine (with excess sulfate) decreases with the growth of the particles." The coagulating action of an alkali chloride is attributed to a driving back of the dissociation of the salt; and a similar action is assumed to account for the precipitation with alkali nitrate.

It will be noted that Pauli's interpretation of the coagulating action as a chemical precipitation process involves the use of the phrases, "peculiar equilibrium between the complex bound and the ionic chlorine" and "peptizing action of the undischarged complex." It would be interesting to know just how Pauli visualizes the "peculiar equilibrium" relations and the "peptizing" action referred to.

Even if one disregards the objections above mentioned, the Pauli mechanism appears inadequate to account reasonably for all the phenomena observed in the titration of ferric oxide sols. A few instances may be mentioned. First of all, it seems altogether improbable that the alleged complex salts of such widely varying anions as sulfate, oxalate, and chromate should all possess practically the same solubility and so precipitate at the same concentration of added electrolyte. Nor is there any reason for supposing that the solubility of the alleged complex trivalent ferricyanide and citrate should be appre-

[189] Kolloid-Beihefte, **17,** 291 (1923)

ciably less than that of the divalent complexes.   Moreover, it is diffi-
cult to explain, on the basis of solubility relationships, why potassium
oxalate and potassium ferricyanide, say, which must be assumed to
form salts of widely varying solubility, should give chloride displace-
ment curves which follow an almost identical course until the pre-
cipitation concentration of the trivalent ion is approached.   Finally,
the present author does not think that the time has yet arrived when
anything can be gained by applying the term salt to a complex formed
when a positively charged particle of variable composition takes up
a given negative ion in varying amounts depending upon the conditions
of preparation of the particle.

Heat of Coagulation.   The change in dispersity of ferric oxide
during coagulation does not involve a measurable heat effect.   The
precise investigations of Mathews and Browne[190] show that the heat
effects during precipitation of sols of low purity are due to dilution of
the ferric chloride and hydrochloric acid in the sols, to mixing of these
electrolytes with the coagulating electrolyte, and to changes in the
adsorption equilibria.   The absence of a heat effect on coagulation
indicates either a very low interfacial tension between hydrous ferric
oxide and water, or no appreciable change in specific surface during
coagulation.   In support of the latter viewpoint, Bradfield[31] showed
that so-called "irreversible" coagula could be repeptized by thorough
washing in the centrifuge.   Apparently, coagulation by electrolytes
is not accompanied by growth of the primary colloidal particles, but
the latter merely agglomerate into clumps without occasioning very
marked decrease in the specific surfaces.

Action of Non-electrolytes.   The addition to ferric oxide sol of
such capillary-active non-electrolytes as camphor, thymol, urethane,
phenol, acetone, and methyl, ethyl, propyl, and isobutyl alcohols, in
not too large amounts, sensitizes the sol toward the action of elec-
trolytes, especially those with univalent precipitating ions,[191] the
effect decreasing with increasing valence of the precipitating ion.[192]
Sufficiently high concentrations of the alcohols appear to exert a
stabilizing action toward sodium chloride.[193]   From a survey of the
influence of foreign non-electrolytes on the stability of lyophobic sols

[190] J. Am. Chem. Soc., **43**, 2336 (1921); Browne: **45**, 297 (1923).

[191] Freundlich and Rona: Biochem. Z., **81**, 96 (1917); Matsuno: **150**, 159 (1924);
Kruyt and van Duin: Kolloid-Beihefte, **5**, 289 (1913); Weiser: J. Phys. Chem., **28**,
1253 (1924).

[192] Dumanskii, Granskaya, and Lonskaya: J. Gen. Chem. (U.S.S.R.) **1**, 295;
Dumanskii and Kharin: 937 (1931).

[193] Janek and Jirgensons: Kolloid-Z., **41**, 40 (1927).

generally, it was concluded[194] that the facts can be accounted for at least qualitatively by considering: (1) the effect on the dielectric constant of the medium, (2) the effect on the degree of ionization of the electrolytes present, and (3) the effect on the selective adsorption of precipitating and stabilizing ions by the colloidal particles. All these factors are measurable and are known to have an effect. Chaudhury[195] believes that the change in interfacial tension between the particles and the surrounding medium will have an important effect on the tendency of the particles to coalesce. Although this may be true, it appears inadvisable to attribute too much effect to a factor that cannot be measured, until it has been shown that the measurable factors mentioned above are inadequate to explain the observed facts.

Coagulation by Sols—Mutual Coagulation

When suitable amounts of two sols of opposite sign are mixed, complete mutual coagulation takes place. Thus when a positive ferric oxide sol is mixed with a negative sol such as platinum, silica, stannic oxide, arsenic trisulfide, and molybdenum blue, both sols coagulate completely within a certain range. This is ordinarily attributed to the mutual discharge of the electrically charged particles of opposite sign with subsequent agglomeration into clumps that settle out. The observations of Biltz[196] are commonly cited to show that the action is determined only by the charge on the particles and not at all by their nature.[197] Thus a comparison of the precipitating action of a series of sols is said to disclose that, although the optimum amount of positive sols required to precipitate negative sols varies, the order is always the same. Bancroft[198] pointed out that this deduction from Biltz's data is not justified. Wintgen and Löwenthal[199] state the generally accepted view in another way when they say that the mutual precipitation of oppositely charged sols is a maximum when the concentrations of the sols expressed in equivalent aggregates are the same, that is, when equal numbers of charges of opposite sign are mixed. This rule was likewise found not to hold when a highly dispersed sol of one sign is mixed with a coarser sol of opposite sign.

[194] Weiser and Mack: J. Phys. Chem., **36**, 101 (1930).

[195] J. Phys. Chem., **32**, 1485 (1928).

[196] Ber., **37**, 1095 (1904).

[197] Freundlich: "Kapillarchemie," 402 (1909); Thomas: Bogue's "Colloidal Behavior," **1**, 325 (1924).

[198] J. Phys. Chem., **19**, 363 (1915).

[199] Z. physik. Chem., **109**, 391 (1924); Lottermoser and May: Kolloid-Z., **58**, 61 (1932).

Lottermoser[200] observed that complete coagulation of positively charged silver iodide containing a slight excess of silver nitrate, and negatively charged silver iodide containing a slight excess of potassium iodide, was obtained when the excess of silver nitrate in one sol is just equivalent to the excess of potassium iodide in the other. This suggests that interaction between the stabilizing ions is the cause of the mutual coagulation of oppositely charged sols. In line with this, Freundlich and Nathansohn[201] found colloidal arsenic trisulfide sol and Odén's sulfur sol to be unstable in the presence of each other. Since both sols are negatively charged, this instability cannot be due to mutual electrical neutralization; it was found to result from interaction between the stabilizing electrolytes of the two sols, hydrogen sulfide and pentathionic acid. Following up the above observations, Thomas and Johnson[202] attributed the mutual coagulation in other cases primarily to chemical interaction of the stabilizing electrolytes in the sols. This cannot be generally true since numerous cases of mutual coagulation of sols are known where interaction between the peptizing agents is impossible or improbable.[203]

From observations on the mutual coagulation of several positive sols (including the hydrous oxides of iron and chromium) and negative sols of varying purity, it was found that the zone of mutual coagulation may be very narrow or quite broad.[203] Moreover, when a given series of positive sols is arranged in order of the optimum concentration for mutual coagulation on mixing with negative sols, the order of the positive sols may vary widely with different negative sols. To account for this behavior it was concluded that the precipitating power of positive sols for negative sols is not determined exclusively by the charge on the particles. Other factors that may come in are: (1) mutual adsorption of colloidal particles that is independent of the charge resulting from adsorbed ions, (2) the presence of precipitating ions as impurities in the sols, and (3) interaction between the stabilizing ions.

Similar phenomena in the mutual coagulation process have been noted by Hazel and McQueen[204] in migration studies on mixtures of positive and negative sols with and without the addition of electrolytes. They attribute the mutual coagulation primarily to mutual

[200] Kolloid-Z., **6**, 78 (1910)

[201] Kolloid-Z., **28**, 258; **29**, 16 (1921).

[202] J. Am. Chem. Soc., **45**, 2532 (1923); Bahl: Kolloid-Z., **59**, 60 (1932).

[203] Weiser and Chapman: J. Phys. Chem., **35**, 543 (1931); **36**, 714 (1932).

[204] J. Phys. Chem., **37**, 553, 571 (1933).

adsorption of the oppositely charged particles with a consequent unequal redistribution of the total charges around the particles.

Billitzer[205] found that gelatin in acid or neutral solution is a positive sol and precipitates negative sols, but not positive ones such as hydrous ferric oxide; whereas gelatin in ammoniacal solution is a negative sol and precipitates hydrous ferric oxide. No precipitate is thrown down, however, if gelatin is first added to colloidal ferric oxide, followed by the addition of ammonia. In the latter case, we get a stable mixture of positive sols changed simultaneously to a stable mixture of negative sols by the addition of hydroxyl ions.

Brossa and Freundlich[206] studied the precipitation and repeptization of colloidal albumin by means of colloidal ferric oxide in the presence of electrolytes. The amount of albumin thrown down by the ferric oxide sol decreases with decreasing concentration of electrolytes until eventually only a slight turbidity results which disappears on adding a sufficient amount of ferric oxide sol. Obviously, the colloidal ferric oxide adsorbs and so keeps the colloidal albumin in solution. The ferric oxide-albumin sol formed in this way is positively charged but is much more sensitive than the original sol. The sensitivity is at its maximum when the ferric oxide has adsorbed all the negative albumin sol that it can hold, without precipitation taking place. With increasing concentrations of ferric oxide sol, the sensitivity falls off, approaching that of the pure positive sol. If instead of adding an electrolyte to a ferric oxide-albumin sol, an albumin sol containing an electrolyte is precipitated with ferric oxide sol, the relationships are identical in many respects, particularly in the amount of albumin adsorbed by the ferric oxide. Serums sensitize ferric oxide sol to varying degrees, but the sensitizing effect of normal serum is greater than that of therapeutic serums.[207]

FERRIC OXIDE JELLIES

Although hydrous ferric oxide is usually thrown down as a gelatinous precipitate, jellies may be prepared by coagulation of a sol under suitable conditions. Thus, Grimaux[208] added to an excess of water an alcoholic solution of ferric ethylate which hydrolyzed very rapidly,

[205] Z. physik. Chem., **51**, 148 (1905); *cf.* Mutzenbecher: Biochem. Z., **243**, 113 (1931).

[206] Z. physik. Chem., **89** 306 (1915); Pauli and Flecker: Biochem. Z., **41**, 479 (1912); Freundlich and Lindau: **202**, 236 (1928); **208**, 100 (1929).

[207] Achard, Boutaric, and Morizot: Compt. rend., **195**, 9 (1932).

[208] Compt. rend., **98**, 105, 1434 (1884).

forming a sol. The sol was similar to Graham's, but the particles were probably much smaller on account of the more rapid rate of hydrolysis.[209] The sol coagulated spontaneously on standing for some time at room temperature, and more rapidly on heating or by the addition of electrolytes such as carbonic, sulfuric, and tartaric acids; the nitrate, chloride, and bromide of potassium; the chlorides of sodium and barium; etc. The coagulum formed in every case was a transparent jelly, provided the sol was not agitated during the process of coagulation. Even with quite dilute sols the jelly was firm, but contraction took place, very slowly in the cold and more rapidly at high temperatures.

Ferric oxide jellies may be prepared also by slow removal of the peptizing agent by dialysis. Thus Grimaux[97] obtained a firm jelly by dialysis of a negative sol prepared by peptization of the hydrous oxide with alkali in the presence of glycerol. If ammonia was used instead of alkali, and the sol exposed to the air, the slow loss of peptizing agent by evaporation resulted in the precipitation of a jelly. Grimaux's observations were confirmed by Fischer,[210] who prepared a firm jelly on prolonged dialysis of a sol containing but 1% of iron.

With colloidal ferric oxide, as with a number of other sols, slow uniform precipitation throughout the entire solution produces a jelly, whereas rapid uneven precipitation results in contraction and the consequent formation of a gelatinous precipitate. As compared with the usual Graham sol, Grimaux's colloid is much more easily thrown down in the form of a jelly. This is accounted for by the fact that a sol formed by rapid hydrolysis in the cold will contain finer and more hydrous particles than one formed by prolonged dialysis in the cold or shorter dialysis in the hot. For the same reason, the coagulum from the Graham sol is much more hydrous and bulky than that obtained from a Péan de St. Gilles sol.

Sol-gel Transformation—Thixotropy. If a suitable amount of electrolyte is added to a Graham sol containing 6 to 10% ferric oxide and the mixture is allowed to stand quietly, it sets to a jelly that is no more cloudy than the original sol. If the jelly is shaken, a sol is re-formed which will set again on standing.[211] This phenomenon which is called thixotropy (p. 23), may be repeated as often as desired provided the amount of electrolyte used is not too great. In the latter event shaking the jelly gives a gelatinous precipitate rather than a

[209] Cf. Wagner: Kolloid-Z., **14**, 150 (1914).

[210] Biochem. Z., **27**, 223 (1910).

[211] Schalek and Szegvari: Kolloid-Z., **32**, 318; **33**, 326 (1923).

sol.[212] Ultrasonic waves will liquefy a thixotropic jelly, the change starting at the air-gel interface.[213]

The time required for the sol-gel transformation—the setting time—is an approximate measure of the thixotropic behavior. The logarithm of the setting time was found to be inversely proportional to the temperature and to the concentration of coagulating electrolyte. As would be expected, for a given concentration of electrolyte the setting time is greater the higher the valence of the precipitating anion.

Freundlich and his pupils[214] have investigated extensively the effect of different materials on the thixotropic behavior. Hydroxyl-holding, hydrophilic materials like amino acids and sugars increase the setting time in the presence of a given amount of coagulating electrolyte. Increasing the hydrogen ion concentration decreases the setting time by rendering the sol relatively more stable. Certain substances which sensitize the sol toward electrolytes, such as gelatin, agar, and saponin, decrease the setting time.

Ultramicroscopic observation of the gel-sol change showed no formation of secondary particles and no change in the average distance between the particles. The reversible gel-sol transformation consists in the breaking and subsequent realignment of the orienting forces among the particles. Kistler[215] believes that the phenomenon is most readily explained by assuming some form of oriented anisotropy of the water, probably chains of water molecules extending out from the surface of each particle and tending to hook in with neighboring particles. It is essential that the particles do not age on standing so that they fail to coalesce after having been broken apart.

By heating a 10% Fe_2O_3 sol to 80°, Rabinerson[216] obtained a thixotropic gel which changed to a sol on standing at room temperature. The gelling at higher temperatures is probably due to hydrolysis of the stabilizing electrolyte, ferric chloride, with the consequent lowering of the ζ-potential; and the subsequent liquefaction at room temperature, to the reversal of the hydrolysis.

[212] Freundlich and Rawitzer: Kolloid-Beihefte, **25**, 235 (1927).

[213] Freundlich, Rogowski, and Söllner: Z. physik. Chem., **A160**, 469 (1932).

[214] Freundlich and Rosenthal: Z. physik. Chem., **121**, 471 (1926); Freundlich and Rawitzer: Kolloid-Beihefte, **25**, 235 (1927); Freundlich and Söllner: Kolloid-Z., **45**, 348 (1928).

[215] J. Phys. Chem., **35**, 815 (1931); cf. Bary: Compt. rend., **196**, 183 (1933).

[216] Kolloid-Z., **66**, 303 (1934).

HYDROUS FERROUS HYDROXIDE

Hydrous ferrous hydroxide is precipitated as a snow-white gel when an alkali or ammonia is added to a solution of a ferrous salt. It is also obtained by hydrolysis of a solution of $Fe(HCO_3)_2$[217] and as snow-white glistening crystals by the action of sunlight on a normal solution of oxygen-free alkaline potassium ferrocyanide.[218] On account of its sensitiveness to minute traces of oxygen, the hydroxide possesses a green color unless special precautions are taken to exclude air during its preparation. Even when dried, the gel oxidizes so readily in the air that the whole mass sometimes becomes incandescent.

The snow-white preparation may be obtained in either of two ways: (1) by mixing the boiled salt and alkali solutions in a special apparatus,[219] in the presence of an oxygen-free neutral gas such as hydrogen or nitrogen; (2) by mixing the two solutions which were boiled while covered with a thick layer of castor oil or vaseline.

The dehydration isobar of the air-dried oxide shows it to contain 1 mol of water combined with 1 mol of FeO.[220] X-ray analysis indicates that the compound is $Fe(OH)_2$ consisting of rhombohedral crystals similar to brucite, $Mg(OH)_2$.[221]

The precipitated oxide undergoes a spontaneous change of some kind on aging. Thus Baudisch and Welo[222] made the important observation that the freshly precipitated compound yields Fe_3O_4 or α-$Fe_2O_3 \cdot H_2O$ or in certain cases γ-$Fe_2O_3 \cdot H_2O$ when oxygen is admitted, but never Fe_2O_3. On the other hand, a precipitate that has been aged 4 days in a neutral solution in the absence of air yields, on oxidation, α-Fe_2O_3 together with a small amount of γ-Fe_2O_3 as evidenced by a weak ferromagnetism. Baudisch and Welo[67] point out that these findings may help to explain the difference between fresh and aged ferrous hydroxide as a reducing agent in the reduction of alkali nitrates.[223] The freshly precipitated hydroxide reduces alkali nitrates to nitrites and oxidizes oxidizable substances such as lactic acid to peruvic acid and uracil to isobarbaturic acid, but only

[217] Baudisch: Naturwissenschaften, **16**, 543 (1928).

[218] Baudisch and Bass: Ber., **55B**, 2699 (1922).

[219] Baudisch and Welo: J. Biol. Chem., **64**, 753 (1925).

[220] Hüttig and Möldner: Z. anorg. Chem., **196**, 177 (1931).

[221] Natta and Casazza: Atti accad. Lincei (6) **5**, 803 (1927); Natta: Gazz. chim. ital., **28**, 355 (1928).

[222] Naturwissenschaften, **21**, 659 (1933).

[223] Baudisch and Mager: Biochem. Z., **107**, 1 (1920); Baudisch: Ber., **54B**, 406 (1921); Baudisch and Welo: J. Biol. Chem., **61**, 261 (1924); **64**, 753 (1925).

in the presence of molecular oxygen. In the absence of oxygen either with or without nitrate, the hydroxide remains snow-white indefinitely, showing that it does not dissociate water into hydrogen and oxygen. After long standing the white hydroxide will neither reduce nitrates nor oxidize lactic acid and uracil even in the presence of oxygen; but it will undergo oxidation itself, giving ferric oxide.

To explain the above observations, Baudisch and Welo assume that the aging of the freshly prepared hydrous oxide involves a transformation in which the water is bound in another way. Since the oxidation of the aged ferrous hydroxide yields ferric oxide and no hydrate whereas the oxidation of the fresh oxide yields γ-$Fe_2O_3 \cdot H_2O$ or Fe_3O_4, it is suggested that the following process takes place: $Fe(OH)_2 \rightarrow FeO \cdot H_2O$. In view of the fact that the fresh oxide in the presence of oxygen can reduce nitrates and oxidize certain organic compounds at room temperature, it is probable that the fresh precipitate in the presence of oxygen dissociates water as follows: $H_2O \rightarrow H^+ + OH^-(H_2O_2)$. Since the aged preparation brings about neither oxidation nor reduction, it is suggested that the water which is dissociated into activated hydrogen and oxygen is not the adsorbed or solvent water but is the labile water which disappears on aging owing to the transformation from hydroxide to hydrated oxide. This hypothesis appears plausible except that aged preparations give the x-ray pattern for a hydroxide rather than a hydrated oxide. One may avoid this difficulty by assuming that the freshly formed gel is hydrous FeO or hydrous $FeO \cdot H_2O$ which is transformed to $Fe(OH)_2$ on aging. It should be possible to determine whether any such transformation takes place by comparing the x-radiogram from the moist gel immediately after precipitation with that of the aged preparation.

Even aged ferrous hydroxide dissociates water into hydrogen at temperatures above $200°,$[224] and the thermal dehydration of the compound yields hydrogen possibly in accord with the reaction: $3Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O + H_2.$[220]

Whitman, Russell, and Davis[225] found that the rate of corrosion of iron in salt solutions parallels the solubility of ferrous hydroxide in these solutions. It is suggested that this is due to changes in film protectivity with the solubility of the ferrous salt.

Ferrous Hydroxide Sol. A sol of ferrous hydroxide results on washing, with the aid of the centrifuge, the white precipitate thrown

[224] Goldberg: Dissertation, Dresden (1914).
[225] J. Am. Chem. Soc , **47,** 70 (1925); *cf.* Friend: J. Chem. Soc., **119,** 932 (1921).

down from a ferrous chloride solution with gaseous ammonia in a vacuum apparatus.[226]   When pure the sol is white with a reddish opalescence in transmitted light.   It is positively charged and behaves toward electrolytes like ferric oxide sol.   Since the hydroxide possesses an appreciable solubility, the sol is relatively instable, the particles growing and agglomerating to the point where they settle out after standing a few days.   .

An impure green sol is formed by electrical disintegration of an iron wire immersed in a dilute gelatin solution contained in a high, narrow cylinder.[227]

HYDROUS FERRO-FERRIC OXIDE

Gelatinous ferro-ferric oxide, Fe_3O_4, is obtained by adding alkali to a solution containing equivalent amounts of ferrous and ferric salts.[228]   If washed and dried out of contact with air it is a magnetic, brownish black mass containing an indefinite amount of water, as evidenced by the smooth course of the dehydration isobar[220] and by the fact that the x-ray diffraction pattern of the hydrous precipitate is the same as that for the mineral magnetite, Fe_3O_4.[229]

Hydrous Fe_3O_4 rather than hydrous Fe_2O_3 is obtained by oxidation of ferrous hydroxide provided the rate of supply of oxygen is low and the medium is alkaline.   It is not immediately obvious why oxidation is retarded by a high hydroxyl ion concentration[230] since it is well known that ferrous hydroxide is a stronger reducing agent in an alkaline medium.   Krause[231] explains this apparent anomaly by pointing out that hydrous Fe_2O_3 [or $Fe(OH)_3$, as he writes it] which is the primary product of the oxidation of $Fe(OH)_2$, has an isoelectric point at $pH = 5.2$.   It therefore assumes an acid character in an alkaline medium and reacts with the still unionized, strongly basic $Fe(OH)_2$ (isoelectric point at $pH > 11.5$) to form ferrous ferrite, $FeO \cdot Fe_2O_3$ or Fe_3O_4, in accord with the reaction:

$$Fe(OH)_2 + Fe_2O_3 \cdot H_2O \rightarrow FeO \cdot Fe_2O_3 + 2H_2O.$$
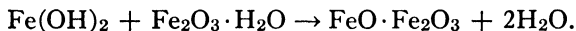
This reaction is favored by supplying the oxygen very slowly and by working at the boiling temperature which favors the combination and,

[226] Deiss and Schikorr: Z. anorg. Chem., **172**, 35 (1928).

[227] Schmauss: Physik. Z., **6**, 506 (1905).

[228] Lefort: Compt. rend., **34**, 488 (1852); **69**, 179 (1869).

[229] Welo and Baudisch: Phil. Mag. (7) **3**, 396 (1927); Naturwissenschaften, **14**, 1005 (1926).

[230] Miyamoto: Bull. Chem. Soc., Japan, **2**, 40 (1927).

[231] Z. anorg. Chem., **174**, 145 (1929); Krause and Tulecki: **195**, 228 (1931).

at the same time, tends to diminish the oxygen supply. At low temperatures and with a large supply of oxygen, the rate of oxidation to ferric oxide is so high and the rate of combination of the ferrous and ferric compounds is so low that little or no $FeO \cdot Fe_2O_3$ is formed.

During the oxidation of $Fe(OH)_2$ to Fe_3O_4 a green intermediate product is always observed. Since this apparently follows the momentary appearance of red hydrous Fe_2O_3, Deiss and Schikorr[232] assume that the green product is an intermediate compound, possibly $2FeO \cdot Fe_2O_3$, but they have no direct experimental evidence that such is the case. In this connection Bancroft and Cunningham[233] showed that, in alkali borate melts, ferrous oxide is colorless, ferric oxide is yellow, and certain mixtures of ferrous and ferric oxides are blue. The greens are due to a mixture of blue and yellow. It is suggested that the blue is due to a blue modification of ferric oxide stabilized by ferrous oxide, the required amount varying with the other substances in the glass. In the absence of confirmatory evidence, this suggestion is not completely satisfactory.

Since the formation of Fe_3O_4 by oxidation of $Fe(OH)_2$ is a slow process involving recrystallization, the crystals are large and well formed and give sharp x-ray diffraction lines. On the other hand, the crystals formed by the simultaneous precipitation of ferrous and ferric ions are thrown down so rapidly that they are relatively small and give more diffuse x-ray diffraction lines. As already noted, the patterns from the synthetic products are the same as from the mineral magnetite.

The magnetic properties of magnetites formed by precipitation and by oxidation of $Fe(OH)_2$ have been studied by Welo and Baudisch.[234]

[232] Z. anorg. Chem., **172**, 32 (1928).
[233] J. Phys. Chem., **34**, 1 (1930).
[234] Phil. Mag. (7) **3**, 396 (1927).

CHAPTER III

THE HYDROUS OXIDES OF ALUMINUM, GALLIUM, INDIUM, AND THALLIUM

HYDROUS ALUMINUM OXIDE

Aluminum oxide, unlike ferric oxide, forms both monohydrates and trihydrates. Moreover, the brown ferric oxide gel is a hydrous oxide whereas the gelatinous precipitate thrown down from a solution of aluminum salt with ammonia is hydrous alumina monohydrate. Accordingly, it seems advisable to review the evidence for the existence of the several alumina hydrates before considering the composition and properties of the gelatinous precipitate.

ALUMINA HYDRATES

ALUMINA TRIHYDRATES

Two crystalline forms of $Al_2O_3 \cdot 3H_2O$ are known: γ-$Al_2O_3 \cdot 3H_2O$ or gibbsite which occurs in nature and has been prepared synthetically; and a metastable synthetic product, α-$Al_2O_3 \cdot 3H_2O$ or bayerite. These compounds result from the hydrolysis of alkali aluminate solutions under suitable conditions. Thus Bonsdorff[1] and Bayer[2] saturated sodium hydroxide solution with gelatinous alumina and allowed the solution to stand in a closed vessel or exposed to the air until crystals appeared. Similarly, Goudriaan[3] dissolved aluminum in sodium hydroxide and allowed the solution to stand in the air; and Fricke[4] passed carbon dioxide slowly into cold alkali aluminate solution or slowly hydrolyzed the aluminate by dilution. Fricke emphasized that a product which gives an x-radiogram identical with the mineral gibbsite is obtained only when the separation from the aluminate takes place quite slowly.[5] On the other hand, if the sepa-

[1] Pogg. Ann., **27**, 275 (1833).
[2] Chem.-Ztg., **12**, 1209 (1889).
[3] Proc. Akad. Sci. Amsterdam, **23**, 129 (1921).
[4] Z. anorg. Chem., **175**, 249 (1928); **179**, 287 (1929); cf. de Schulten: Compt. rend., **122**, 1428 (1896); Achenbach: Chem. Erde, **6**, 312 (1931).
[5] Fricke and Jucaitis: Z. anorg. Chem., **191**, 132 (1930).

ration takes place relatively quickly, in hours or a few days, an isomeric form of the trihydrate—α-$Al_2O_3 \cdot 3H_2O$—is obtained which gives a distinctive x-radiogram.[6]   Diagrams of the x-ray patterns of the two isomers are given in Fig. 16 a and b. α-$Al_2O_3 \cdot 3H_2O$ is metastable with respect to γ-$Al_2O_3 \cdot 3H_2O$ and goes over to the latter spontaneously in the course of a few weeks' contact with dilute alkali.

A number of people[7] have obtained synthetic trihydrates which gave x-ray diagrams unlike γ-$Al_2O_3 \cdot 3H_2O$.   Since these differed among themselves but were similar in certain respects to the pattern
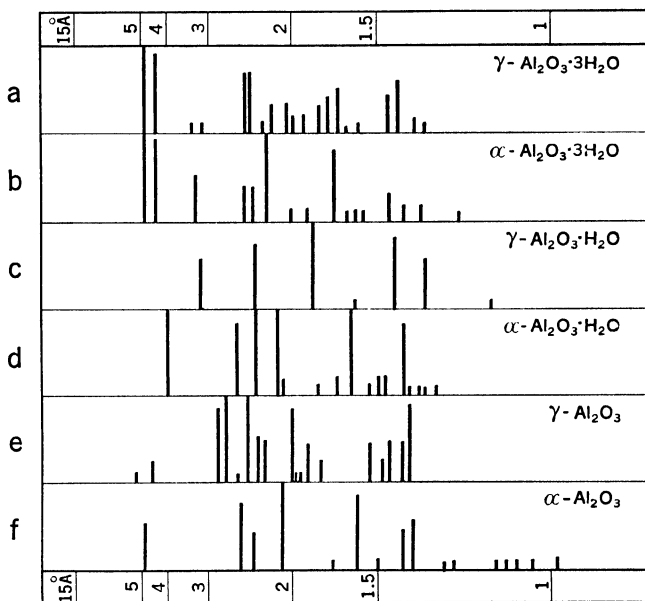
FIG. 16.—Diagrams of the x-ray diffraction patterns of aluminas and their hydrates.

from gibbsite, it was believed at one time[8] that the product known as α-$Al_2O_3 \cdot 3H_2O$ was a mixture of varying amounts of γ-$Al_2O_3 \cdot 3H_2O$ and böhmite (γ-$Al_2O_3 \cdot H_2O$).   It is now known, however, that samples of the metastable α-$Al_2O_3 \cdot 3H_2O$ are likely to contain more or less of

[6] Fricke and Wullhorst: Z. anorg. Chem., **205**, 131 (1932); *cf.* Fricke and Meyring: **214**, 269 (1933).

[7] Fricke: Z. anorg. Chem., **166**, 252 (1927); Hansen and Brownmiller: Am. J. Sci. (5) **15**, 228 (1929); Rooksby: Trans. Ceram. Sci., **28**, 399 (1929); Damerell: J. Phys. Chem., **35**, 1061 (1931); Damerell, Hovorka, and White: **36**, 1255 (1932).

[8] Weiser and Milligan: J. Phys. Chem., **36**, 3011 (1932); *cf.*, *also*, Achenbach: Chem. Erde, **6**, 312 (1931).

the stable isomer, and that this accounts for the differences in the bayerite patterns obtained by different investigators and the presence in them of lines corresponding to $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

The dehydration isobars at 100-mm pressure for $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ obtained by Fricke and Severin[9] are given in Fig. 17. The data from which these curves were constructed were obtained with unusual care to ensure an equilibrium state. At the lower temperatures several weeks were required to get a single point, and the value was taken only after the system remained
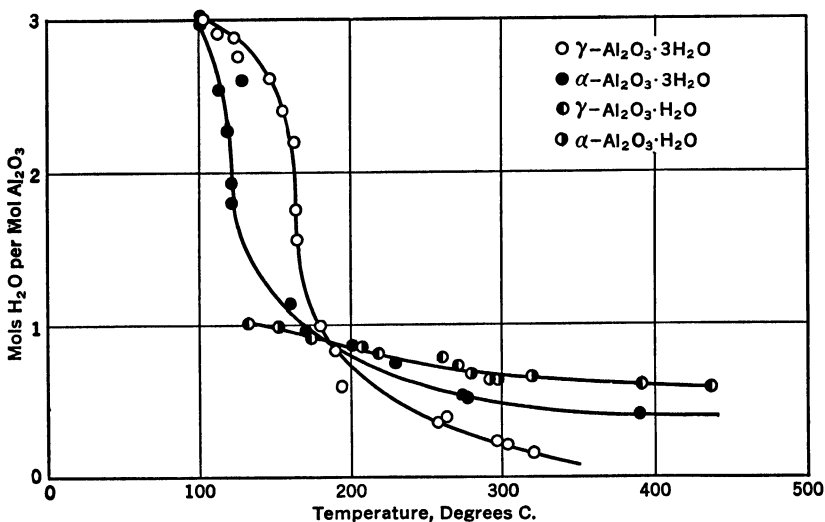
FIG. 17.—Dehydration isobars of alumina hydrates.

in equilibrium 8–25 days. It will be noted that both compounds have the composition $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ up to approximately 120°. This would not be expected if the bayerite were a mixture of $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ with the $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Moreover, since bayerite decomposes rapidly at a lower temperature than $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and since böhmite decomposes at a higher temperature than $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, it seems unlikely that bayerite can be a mixture of $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and böhmite.

ALUMINA MONOHYDRATES

Two monohydrates of alumina exist: $\alpha\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or diaspore, which occurs in nature, and $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, which is called böhmite

[9] Z. anorg. Chem., **205**, 287 (1932).

since Böhm[10] using x-ray diffraction analysis first detected it in certain natural bauxites and also showed that it was present in the slimy, voluminous mass formed by heating the precipitated gel for a few hours at 200° in an autoclave.

A product which gives the same x-radiogram first observed by Böhm results from the isobaric dehydration of γ-$Al_2O_3 \cdot 3H_2O$. By referring to Fig. 17 it will be seen that the dehydration curves show no break at a composition corresponding to $Al_2O_3 \cdot H_2O$. This behavior was reported first by L. H. Milligan.[11] In the author's laboratory[12] a gibbsite dehydrated to a composition below $Al_2O_3 \cdot$-$0.5H_2O$ gave the böhmite x-ray pattern free from the lines of other substances. Attempts to reduce the water content to zero changed the product to γ-Al_2O_3.

In the light of the above work there can be little question about the facts. The monohydrate formed by the decomposition of γ-$Al_2O_3 \cdot$-$3H_2O$ does not undergo decomposition at a definite temperature as a real hydrate usually does. Indeed, in the dehydration curve shown in Fig. 19, a sample at 410° C having a composition of approximately $Al_2O_3 \cdot 0.34H_2O$ gave the x-radiogram of γ-$Al_2O_3 \cdot H_2O$ only. This would be impossible if the hydrate were behaving in a normal way. Furthermore, Fricke and Severin's curve for the monohydrate is a typical desorption curve showing no indication whatsoever of a break. It is this sort of evidence which formerly led to the conclusion that the alleged monohydrate was not a true hydrate but an alumina with adsorbed water.

The only evidence advanced by Rooksby[13] in support of the view that the initial product of the thermal dehydration of γ-$Al_2O_3 \cdot 3H_2O$ is a monohydrate, was an analysis of the product. But the dehydration curves of L. H. Milligan, Fricke and Severin, and Weiser and Milligan show that this composition was accidental and could not possibly have been an equilibrium value. More recently, Edwards and Tosterud[14] claim that the compound formed by heating precipitated alumina under pressure analyzes for a monohydrate, gives the γ-$Al_2O_3 \cdot H_2O$ x-ray pattern, and exhibits a thermal arrest in the heating curve. The first two lines of evidence will not definitely distinguish between a monohydrate and a hydrous alumina with the

[10] Z. anorg. Chem., **149**, 206 (1925).

[11] J. Phys. Chem., **26**, 247 (1922).

[12] Weiser and Milligan: J. Phys. Chem., **36**, 3010 (1932); **38**, 1175 (1934).

[13] Trans. Ceram. Soc., England, **28**, 399 (1929).

[14] J. Phys. Chem., **37**, 483 (1933).

right amount of adsorbed water, and an arrest in the heating curve of an oxide-water system does not necessarily indicate the presence of a true hydrate.[15]   In this case the arrest might be offered as evidence of a polymorphic change to γ-Al_2O_3 from some other form of the oxide.   However, preparations which give the γ-$Al_2O_3 \cdot H_2O$ pattern can be obtained in well-defined macroscopic crystals which analyze for monohydrate.   Thus Fricke and Severin obtained it by heating commercial alumina trihydrate to 305–370° at a pressure of 200 atmospheres.   Hüttig and Peter[16] prepared a similar product by heating the trihydrate in a bomb tube at 200 atmospheres.   Particularly good crystals were formed by heating 4–20% $Al(NO_3)_3$ contain-
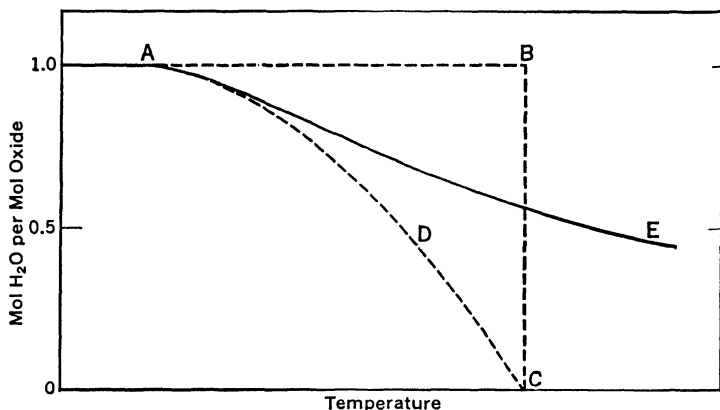
FIG. 18.—Dehydration isobar for a monohydrate which gives a highly hygroscopic dehydration product.

ing up to 20% HNO_3 at 320–360° and 200–300 atmospheres.[17]   In the light of this positive evidence there can be no longer any doubt that böhmite is γ-$Al_2O_3 \cdot H_2O$.   But having reached this conclusion, one is obliged to explain the absence of any sign of a break corresponding to the monohydrate in the dehydration isobars of γ-$Al_2O_3 \cdot 3H_2O$ and γ-$Al_2O_3 \cdot H_2O$.

Application of the phase rule to the two-component system hydrate-oxide-water vapor, shows that the system should be univariant.   The type of isobar is given by the lines AB and BC in Fig. 18.   Theoretically, the curve should drop to zero composition

[15] Huggett: Ann. chim. (10) 11, 447 (1929).
[16] Kolloid-Z., 54, 140 (1931).
[17] Ipatiev: Ber., 63B, 2365 (1930); Ipatiev and Muromzev: 60B, 1981 (1927).

at a definite temperature, but actually the isobars are usually rounded off as shown in the figure by the line ADC. This is due to loss of part of the water below the true decomposition temperature of the mass of the hydrate on account of lattice distortion, strain in the crystals, and variation in crystal size. Now if the oxide formed by the dehydration of the hydrate is highly hygroscopic, it will adsorb most of the water vapor. Hence the actual dehydration measured is the loss of adsorbed water from the oxide. In such cases a bivariant type of curve is to be expected, as shown by the solid line AE in Fig. 18. It is precisely this last type of curve which Fricke and Severin obtained for both α- and γ-Al$_2$O$_3 \cdot$H$_2$O.

The loss of water by a hydrate below a definite decomposition temperature is attributed by Damerell[18] to surface dehydration of extremely minute crystals, without lattice rearrangement. This view is unsatisfactory since one gets a similar form of curve even with macroscopic crystals.

We can now explain the persistence of the x-radiogram of the monohydrate where it would ordinarily not be expected to exist. The x-radiogram for the monohydrate should persist along the broken curve ADC because some monohydrate exists as such and the very highly hydroscopic γ-Al$_2$O$_3$[19] formed by partial decomposition of the former is either amorphous or too finely crystalline to be detected by x-ray analysis.

In a higher hydrate decomposing first into a lower hydrate and finally into the anhydrous substance, it is apparent that, under the conditions noted above, the isobar will fail completely to detect the lower hydrate. In Fig. 19 the theoretical curves for the case of a trihydrate decomposing to a monohydrate and this in tuin to the oxide are given by the broken lines. The actual experimental curve as obtained by Weiser and Milligan is given by the solid line. The composition of the trihydrate remains constant until at point F some water is lost, giving a small amount of water vapor and monohydrate. As this process continues along FKH, all the trihydrate decomposes rapidly, giving monohydrate. Now at this temperature the lower hydrate loses water to point O, and hence the line FKH con-

[18] Damerell: J. Phys. Chem., **35**, 1061 (1931); Damerell, Hovorka, and White: **36**, 1255 (1932).

[19] Baxter and Warren: J. Am. Chem. Soc., **33**, 340 (1911); Dover and Marden: **39**, 1609 (1917); Marden and Elliott: Ind. Eng. Chem., **7**, 320 (1915); Yoe: Chem. News, **130**, 340 (1925); Barnitt, Derr, and Scripture: Ind. Eng. Chem. (Anal. Ed.) **2**, 355 (1930); Bower: Bur. Stand. J. Research, **12**, 241 (1934).

tinues past the theoretical composition of the monohydrate to the point
O. This decomposition of the monohydrate gives the highly adsorp-
tive γ-oxide, the presence of which causes the dehydration to proceed
along the line *HOE* for the reason given above.

Although the case under consideration is unusual it is probably not
unique. The dehydration of any hydrate which yields a sufficiently
hygroscopic product might be expected to give this type of curve. But
in the interpretation of curves of this kind care must be taken to dis-
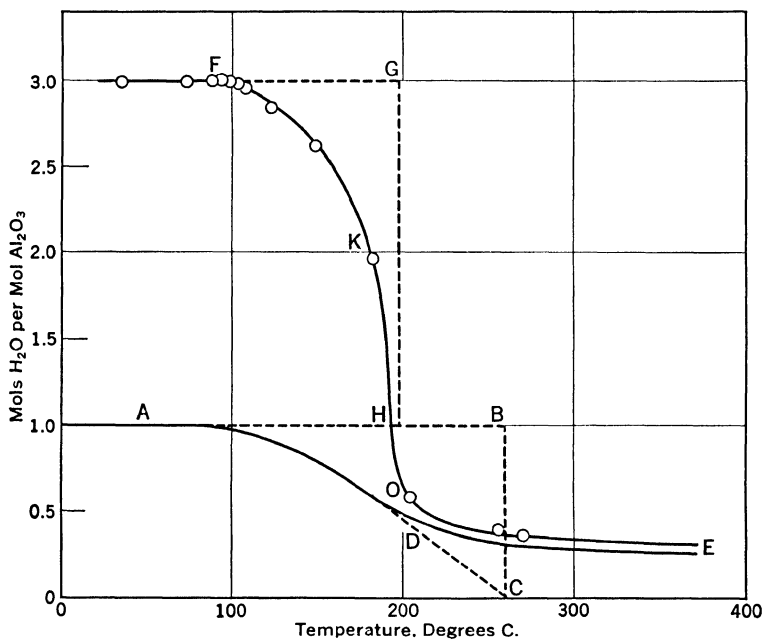
FIG. 19.—Dehydration isobar of γ-Al$_2$O$_3$·3H$_2$O. Solid curve, observed; broken
curve, theoretical.

tinguish between hygroscopicity resulting from strong adsorption and
from the tendency to form a hydrate. The dehydration of gypsum
which yields plaster of Paris as an intermediate product is said by some[20]
to give a curve like *FKHE* rather than like *FGHB*. Work in the author's
laboratory shows that this is not the case; but even if it were, it would
be incorrect to attribute the form of the curve to the adsorbing action
of soluble anhydrate.

The dehydration of γ-Al$_2$O$_3$·3H$_2$O and γ-Al$_2$O$_3$·H$_2$O represent

[20] Linck and Jung: Z. anorg. Chem., **137**, 407 (1924); Balarew: Kolloid-Z., **48**,
63 (1929); Gibson and Holt: J. Chem. Soc., 638 (1933).

extreme cases because of the marked adsorptive capacity of γ-Al_2O_3 for water. If the dehydration product were only moderately hygroscopic it would not prevent the appearance of a point of inflection more or less sharply defined.

Diagrams of the x-ray diffraction patterns of γ-$Al_2O_3 \cdot H_2O$ or böhmite, the mineral diaspore, γ-Al_2O_3 formed during the dehydration of böhmite at about 500°, and α-Al_2O_3 formed by heating the latter to 1000°, obtained in the author's laboratory by Milligan are shown in Fig. 16 *d*, *e*, *f*, and *g*. It will be recalled that in the dehydration of böhmite the pattern persists until the composition is less than $0.5H_2O : 1Al_2O_3$ at a temperature in the neighborhood of 500° when the pattern of γ-Al_2O_3 appears. Obviously the alumina first formed in the dehydration is amorphous or so minutely crystalline that it gives no x-ray diffraction pattern. It is this amorphous or very finely crystalline material which is so hygroscopic.

GELATINOUS ALUMINA

FORMATION AND COMPOSITION

The Precipitated Gel

The addition of ammonia to an aluminum salt solution throws down a highly gelatinous precipitate. If the precipitation takes place in the hot the gel gives the x-ray pattern of γ-$Al_2O_3 \cdot H_2O$.[21] It is usually stated that the gel formed in the cold is amorphous,[22] but this is probably not the case. Certainly if it is amorphous when first formed, it goes to γ-$Al_2O_3 \cdot H_2O$ in a short time. Thus, Rooksby obtained diffuse γ-$Al_2O_3 \cdot H_2O$ lines from a gel thrown down at room temperature, and Havestadt and Fricke found the same thing for a gel precipitated at 0° and washed 8 hours by decantation. It is probable that the failure of some people to get a pattern with the freshly formed gel is due to the limitations of the x-ray apparatus employed. As we shall see, aging the gel in the cold leads to the formation of α-$Al_2O_3 \cdot 3H_2O$ under certain conditions and the ultimate transformation of the α- to γ-$Al_2O_3 \cdot 3H_2O$ under other conditions.

Willstätter and Kraut[23] describe several hydrous aluminas differing in reactivity and adsorptive power by precipitating aluminum sulfate with ammonia under varying conditions. A precipitate

[21] Havestadt and Fricke: Z. anorg. Chem., **188**, 357 (1930).

[22] Böhm: Z. anorg. Chem., **149**, 203 (1925).

[23] Ber., **56B**, 149, 1117 (1923); **57B**, 1082 (1924); **58B**, 2451 (1925); *cf*. Prutton, Maron, and Unger: J. Am. Chem. Soc., **57**, 407 (1935).

formed by mixing 1 l of 1 N $Al_2(SO_4)_3$ at 100° and 1 l of 6 N NH_4OH at 50°, followed by conducting in steam for 5 hours, was a pale yellow plastic mass A; without the steam treatment, it was a very pale yellow plastic mass B; with more dilute ammonia it was a pure white, very voluminous, and very finely divided substance, C.   An intermediate variety b, prepared by the dialysis of aluminum chloride with frequent additions of small quantities of ammonia, was claimed to be related chemically to B but resembled A in adsorptive power; a modified form of C precipitated at 60° had an adsorptive capacity similar to B; and a new form of A[24] claimed to be $Al_2O_3 \cdot 2H_2O$ was obtained by carrying out the precipitation at approximately 50°, washing by decantation 4 times, followed by the addition of 15% ammonia and further washing by decantation until peptization started.   As a result of dehydration experiments with the gels, Willstätter claimed to get various hydrates which gave certain temperature intervals of almost constant water content.   Thus precipitates obtained at low hydroxyl ion concentration and washed with acetone which was tacitly assumed to remove adsorbed water, analyzed approximately for trihydrate; and precipitates obtained with excess ammonia in the hot gave what were assumed to be polyaluminum hydroxides such as $2Al(OH)_3 \cdot H_2O$, $4Al(OH)_3 \cdot 3H_2O$, and so on up to $8Al(OH)_3 \cdot 7H_2O$.   X-ray analysis of the several preparations in the author's laboratory[25] showed that most of Willstätter's alleged hydrates have no existence in fact.   Thus the preparations A, B, C, and new A all gave the x-ray pattern of the monohydrate γ-$Al_2O_3 \cdot H_2O$.   Of course, if the preparations originally γ-$Al_2O_3 \cdot H_2O$ are aged under suitable conditions in the cold, lines corresponding to α-$Al_2O_3 \cdot 3H_2O$ or γ-$Al_2O_3 \cdot 3H_2O$ may appear also in the x-radiogram. But Willstätter's gels are at the outset essentially γ-$Al_2O_3 \cdot H_2O$ which differ in particle size and in degree of hydration, and hence show marked differences in their behavior toward reagents and in their adsorption capacity for dyes and enzymes.

Although gelatinous alumina is hydrous γ-$Al_2O_3 \cdot H_2O$, the dehydration curve exhibits no point of inflection corresponding to a monohydrate.   The reason for this has already been considered in detail (p. 94).   Thiessen and Thater[26] prepared an electrolyte-free gel by the hydrolysis of aluminum ethylate.   The fresh, highly hydrous

[24] Willstätter, Kraut, and Humme: Ber., **64B**, 1697 (1931).

[25] Weiser and Milligan: J. Phys. Chem., **36**, 3010 (1932); *cf*. Biltz and Lehrer: Z. anorg. Chem., **172**, 304 (1928).

[26] Z. anorg. Chem., **181**, 417 (1929).

gel gave a smooth pressure-composition curve, but an aged, more granular gel showed a point of inflection in the pressure-composition curve corresponding to $Al_2O_3 \cdot 3H_2O$. The fresh gel was probably hydrous γ-$Al_2O_3 \cdot H_2O$, and the aged gel gave the x-ray pattern of α-$Al_2O_3 \cdot 3H_2O$.

Fibrous Alumina

A very voluminous, fibrous-appearing form of alumina is obtained by the action of moist air on amalgamated aluminum.[27] The aluminum, after first etching with sodium hydroxide, is amalgamated by dipping into a solution of mercuric chloride. After washing, the excess moisture is removed and the amalgam placed in the air. If water is not in excess, "fibers" of hydrous alumina grow rapidly from active regions on the surface; if there is too much water, the growth is slimy and the formation of the oxide is slowed down. The oxide is extremely finely divided and possesses a high adsorption capacity.

By a modification of the above procedure Neogi and Mitra[28] claim to get crystals of $Al_2O_3 \cdot 4H_2O$, but this could not be confirmed by the author.

PROPERTIES

Aging

The gelatinous oxide freshly precipitated in the cold dissolves in acids and alkalis, forming salts, and is readily peptized by certain dilute acids and salts. The precipitate thrown down from the hot solution is more dense, less reactive, and less easily peptized. The oxide precipitated in the cold ages fairly rapidly in the hot and more slowly in the cold even under water. Aging in boiling water consists in the growth of crystals and loss of adsorbed water from hydrous γ-$Al_2O_3 \cdot H_2O$. Aging in cold water involves the same processes, but in addition a gradual transformation takes place from γ-$Al_2O_3 \cdot H_2O$ through α-$Al_2O_3 \cdot 3H_2O$ to γ-$Al_2O_3 \cdot 3H_2O$. This process is more rapid in water containing alkali. Since the trihydrate, γ-$Al_2O_3 \cdot 3H_2O$, is insoluble in cold acids and alkalis and is but slowly soluble in hot concentrated hydrochloric acid, it is evident that the decrease in reactivity on aging the gel in the cold is due not only to a change in specific surface but also to the transformation from one crystalline form to another. There is no real justification for assuming the formation of α-, β-, and γ-aluminum hydroxides to account for the differences in

[27] Wislicenus: Z. angew. Chem., 17, 805 (1904); Kolloid-Z., 2, 2nd Supplement' XI (1908).

[28] J. Chem. Soc., 1222 (1927).

physical character, solubility, and peptizability which accompany the aging process. In other words, apart from the transformation from one crystalline form to another, the aging is a continuous and not a stepwise process as Kohlschütter suggests.[29]

The rate of solution of aged precipitated alumina in hydrochloric acid is increased several-fold by the presence of electrolytes with multivalent anions which are strongly adsorbed.[30] This is attributed to the effect of the adsorbed ions on the electrical potential difference at the solid-liquid interface.

A study of the transformation from one crystalline form to another by isobaric dehydration and x-ray diffraction methods led Hüttig[31] to conclude that a continuous series of crystalline hydrates between monohydrate and trihydrate are formed. It is much more probable that the intermediate products are mixtures of γ-$Al_2O_3 \cdot H_2O$, α-$Al_2O_3 \cdot 3H_2O$, and γ-$Al_2O_3 \cdot 3H_2O$ in varying amounts depending on the method of precipitation and treatment of the sample.[32]

Freezing alumina gel a few hours gives a granular product; and repeated freezing and thawing causes more or less of the capillary bound water to be released[33] (cf. p. 29).

Adsorption

The alumina gel plays an important rôle in such technical processes as dyeing and water purification. These processes will be considered in detail in Chapters XV and XVIII and will not be taken up at this point. The adsorption of precipitating ions during the coagulation of sol will be discussed in a later section of this Chapter (p. 112).

Adsorption from Solution. Freshly formed alumina gel adsorbs arsenious acid from solution less strongly than hydrous ferric oxide (p. 36). The adsorption is reversible and falls off rapidly as the gel is aged.[34] The order of adsorbing power of different hydrous oxides and hydroxides for arsenious acid is as follows:

$$Al_2O_3 < Fe_2O_3 < Cr_2O_3 < Cd(OH)_2 < Zn(OH)_2 < Mn(OH)_2.[35]$$
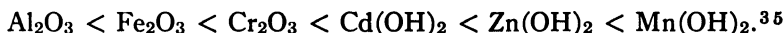
[29] Kohlschütter and Beutler: Helv. Chim. Acta, **14**, 3, 305, 330 (1931).

[30] Tartar, Bryan, and Shinn: J. Am. Chem. Soc., **55**, 2266 (1933).

[31] Hüttig and Wittgenstein: Z. anorg. Chem., **171**, 329 (1928); Hüttig and Kostelitz: **187**, 11 (1930).

[32] Weiser and Milligan: J. Phys. Chem., **36**, 3010 (1932).

[33] Hepburn: Rec. trav. chim., **45**, 326 (1926); Foote and Saxton: J. Am. Chem. Soc., **38**, 599 (1916); **39**, 1108 (1917); cf., also, Lottermoser and Langenscheidt: Kolloid-Z., **58**, 336 (1932).

[34] Yoe: J. Am. Chem. Soc., **46**, 2390 (1924); Sen: J. Phys. Chem., **31**, 686 (1927).

[35] Boutaric and Perreau: J. pharm. chim. (8) **8**, 217 (1928).

The adsorption of potassium halides, nitrate, thiocyanate, sulfate, chromate, dichromate, ferrocyanide, salicylate, oxalate, succinate, and sulfanilate on fibrous alumina was found to follow the Freundlich adsorption equation. In general, the adsorption was greater the higher the valence of the anion, in accord with Schulze's valency rule.[36]

The adsorption of chromate by alumina gel is sufficiently strong to impart a yellow color to the precipitate formed in the presence of alkali chromate or precipitated and subsequently shaken with alkali chromate solution. Charriou[37] found little alkali metal in the precipitate and so attributed the color to the formation of aluminum chromate on the surface of the alumina. There is no justification for this conclusion, and it is probably erroneous. If well-washed alumina is shaken with alkali chromate, the solution becomes alkaline owing to stronger adsorption of acid than of base. The yellow color is due to chromic acid rather than to aluminum chromate. Ishizaka[38] found that potassium dichromate was converted to chromate in the presence of powdered alumina. The explanation of this phenomenon is as follows: The equilibrium in solution between dichromate and chromate ions may be represented by the equation:

$$Cr_2O_7^{--} + H_2O \rightleftharpoons 2H^+ + 2CrO_4^{--}$$
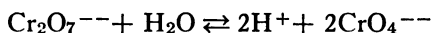
Alumina shows such a strong preferential adsorption for hydrogen ion that the presence of the oxide in a finely divided condition shifts the equilibrium to the right with the formation of chromate ion at the expense of dichromate. Colloidal alumina stabilized by preferential adsorption of hydrogen ion has a comparatively slight effect on the equilibrium.[39]

Adsorbed chromate is displaced but slightly by washing with 5% solutions of the more weakly adsorbed chloride, bromide, iodide, nitrate, or acetate ions; but it is displaced by more strongly adsorbed ions such as carbonate, sulfate, sulfide, oxalate, tartrate, phosphate, or arsenate. Similarly, sulfate is not displaced by weakly adsorbed univalent ions but is displaced by bivalent ions. Charriou generalized that an adsorbed ion is displaced by one of the same kind having the same or a higher valence, but is not displaced by one of lower valence. With two ions of the same valence, the less concentrated is displaced

[36] Ishizaka: Z. physik. Chem., **83**, 102 (1913); cf., *however*, Mehrotra and Dhar: J. Phys. Chem., **30**, 1189 (1926).

[37] Compt. rend., **176**, 679, 1890 (1923); J. chim. phys., **23**, 629 (1926).

[38] Z. physik. Chem., **83**, 97 (1913).

[39] Weiser and Middleton: J. Phys. Chem., **24**, 648 (1920).

the most. These generalizations may be approximately true in certain cases, but they are necessarily not quantitative, since they are based on the erroneous impression that ions of like valences are all adsorbed to the same extent and that trivalent ions are always more strongly adsorbed than bivalent and bivalent ions always more strongly adsorbed than univalent. Generalizations based on Schulze's law are of value only if the limitations of the law are fully recognized.[40]

From the practical point of view, in the quantitative estimation of alumina one may avoid the contamination by such ions as chromate by carrying out the precipitation with NH_4HCO_3 instead of NaOH, or one may remove the adsorbed ion by washing the precipitate with NH_4HCO_3.

Miller[41] investigated the simultaneous adsorption of sulfate and oxalate ions during the precipitation of alumina and concluded that the adsorption was a solid solution phenomenon. This will be discussed in connection with the simultaneous adsorption of sulfate and oxalate by hydrous chromic oxide (p. 144).

If a small amount of ferric salt is added to the test tube containing the precipitate thrown down from an alumina sol by the required amount of ferrocyanide, no Prussian blue is formed until after an appreciable interval of time.[42] This is not due to the slow rate of reaction between ferrocyanide and ferric ion, as a result of the colloidal nature of ferric salt solutions;[43] it is due to the very strong adsorption of ferrocyanide ion which removes it from the field of action. If another strongly adsorbed precipitating ion is added to the sol either before or after precipitation, the ferrocyanide is displaced and the time necessary for the appearance of Prussian blue is diminished appreciably. In the same way, the transformation of Congo blue to Congo red by dilute alkali is slowed down in the presence of hydrous alumina on account of the strong adsorption of Congo blue by the hydrous oxide.[44]

The adsorption by alumina gel of a series of 18 different types of organic compounds discloses that the adsorption is roughly proportional to their acid strengths.[45] Certain salts are hydrolyzed as a

[40] Weiser: J. Phys. Chem., **29**, 963 (1925).

[41] U. S. Pub. Health Repts., **39**, 1502 (1924).

[42] Reitstötter: Kolloid-Z., **21**, 197 (1917); Freundlich and Reitstötter: **23**, 23 (1918).

[43] Vorländer: Kolloid-Z., **22**, 103 (1918).

[44] Bayliss: Proc. Roc. Soc. (London) **84B**, 81 (1912); Weiser and Radcliffe: J. Phys. Chem., **32**, 1875 (1928).

[45] Grettie and Williams: J. Am. Chem. Soc., **50**, 668 (1928).

result of stronger adsorption of acids than of bases by fibrous alumina gel.[46] The order of adsorption of a series of acids by precipitated alumina is: citric > tartaric > oxalic > benzoic.[47]

Organic sulfur compounds such as dimethyl sulfate are strongly adsorbed from petroleum distillates by alumina gel.[48] Alkyl sulfides are likewise removed to a certain extent.[49]

Adsorption from Sol. Negative sols of silver,[50] Prussian blue,[51] and gold[52] are decolorized by shaking with alumina gel. If the gel is freshly formed, a marked adsorption reversal takes place as the gel ages, especially with Prussian blue.

The selective adsorption by alumina of colloidally dispersed organic bodies offers a great many possibilities to the biochemist.[53] Thus enzymes are fractionally adsorbed by the gel, and since the adsorption is at least partly reversible, the phenomena may be used for the isolation and purification of enzymes. Work along this line has been carried on chiefly by Willstätter and his pupils. The results of this work and the important references are contained in his book, "Untersuchungen über Enzyme," Berlin, Vol. I, pages 3–68 (1928).

At low concentrations, egg albumin[54] is adsorbed positively, but the adsorption reaches a maximum and apparently drops to zero in a 9% sol. This behavior is due to relatively stronger adsorption of water than of albumin at the higher concentrations. Koch's tuberculin and Deny's tuberculin can be distinguished by their difference in adsorbability by alumina. Selective adsorption by alumina is recommended for the purification of pepsin and diphtheria antitoxin. The toxin but not the antitoxin of diphtheria is adsorbed by alumina,[55] whereas both the toxin and antitoxin of tetanus are adsorbed. Tetanus lysin is adsorbed slightly, but the antilysin is not adsorbed at all.[56]

[46] Ruegg: Kolloid-Z., **41**, 275 (1927).
[47] Sen: Z. anorg. Chem., **182**, 124 (1929); J. Phys. Chem., **31**, 691 (1927); cf., also, Lachs: Z. physik. Chem., **91**, 159 (1916).
[48] Choudhury and Bagchi: J. Indian Chem. Soc., **5**, 111 (1928).
[49] Borgstrom and McIntire: Ind. Eng. Chem., **23**, 323 (1931).
[50] Biltz and Utescher: Ber., **38**, 2971 (1905).
[51] Wedekind and Fischer: Ber., **60B**, 544 (1927).
[52] Bonnell: Z. anorg. Chem., **169**, 347 (1928).
[53] Euler and Erikson: Z. physiol. Chem., **128**, 1, 9; Euler and Nilsson: **131**, 107 (1923); **134**, 22 (1924).
[54] Rakusin and Braudo: J. Russ. Phys.-Chem. Soc., **48**, 96 (1916).
[55] Cf. Hansen: Compt. rend. soc. biol., **108**, 570 (1931); **111**, 321, 324 (1932).
[56] Kraus and Barbará: Deut. med. Wochschr., **41**, 393 (1915); Zunz: Z. Immunitäts., **19**, (1) 326 (1913).

Adsorption of Gases and Vapors. Attention has been called to the remarkable adsorbing power for water of alumina dehydrated under suitable conditions (p. 95). The partially dehydrated gel is a good adsorbent for the recovery of vapors[57] of gasoline, ether, benzene, the alcohols, sulfur dioxide, ammonia, carbon bisulfide, hexane, toluene, etc. It is not satisfactory for the recovery of such vapors as acetone, acetyl bromide, and acetyl chloride which are catalytically decomposed by it. By comparing the data for the adsorption of benzene and of water by alumina, Munro and Johnson[58] showed that hydration or "chemical" forces play no rôle in the taking up of water by alumina.

From investigations of the relationship between adsorption of water, ethyl alcohol, acetic acid, and ethyl acetate and esterification at oxide surfaces, Pearce[59] concludes that in the catalytic process the alcohol and acetic acid vapors must be adsorbed simultaneously. Moreover, the catalytic effect of different oxides is in the order: $ThO_2 > Al_2O_3 > WO_3 > ZrO_2$, which is the same as the order of the dehydrating power of these oxides toward alcohol and the reverse of the order of adsorption of ethyl acetate. The mechanism of the catalytic hydrogenation and dehydrogenation processes at the surface of oxide catalysts has been considered elsewhere.[60]

In a study of the adsorption of propylene by alumina, Morris and Maass[61] showed the absence of discontinuity in adsorption processes with a change from vapor to gaseous state. On the other hand, adsorption does not occur from the liquid state, and the adsorption curve exhibits a marked discontinuity with a change from liquid state to gaseous state.

ALUMINA HYDROSOLS

The hydrosols of alumina are in general positively charged. The titration curves of aluminum salts with alkali hydroxide indicate the formation of colloidal alumina and not alkali aluminate.[62] The addi-

[57] Munro and Johnson: Ind. Eng. Chem., **17**, 88 (1925); Perry: J. Phys. Chem., **29**, 1462 (1925).

[58] J. Phys. Chem., **30**, 172 (1926); Can. J. Research, **10**, 321 (1934).

[59] Pearce and Alvarado: J. Phys. Chem., **29**, 265 (1925); Pearce and Rice: **33**, 701 (1929).

[60] Vol. I, p. 227; *see, also,* Bancroft and George: J. Phys. Chem., **35**, 2943 (1931); for a recent study of activated adsorption of hydrocarbons on chromic oxide *see* Howard and Taylor: J. Am. Chem. Soc., **56**, 2259 (1934).

[61] Can. J. Research, **9**, 240 (1933).

[62] Davis and Farnham: J. Phys. Chem., **36**, 1057 (1933); *cf., however,* Hildebrand: J. Am. Chem. Soc., **35**, 864; Blum: 1499 (1913); **36**, 2383 (1914); Slade and Polack: Trans. Faraday Soc., **10**, 150 (1914).

tion of excess alkali hydroxide to the gelatinous oxide may result in the transient formation of a negative sol, but this is followed by the formation of alkali aluminate which subsequently decomposes giving relatively large crystals of $Al_2O_3 \cdot 3H_2O$. Similarly, the precipitation of aluminum as the hydrous oxide in excess ammonia is not quantitative, probably on account of the solvent action of the ammonia rather than on account of its peptizing action.[63] However, Lottermoser and Frederich[64] prepared a very readily peptized hydrous oxide by adding aluminum chloride in small increments to $N/10$ ammonia solution stirred by air saturated with ammonia followed by purification by dialysis. This gel is peptized by dilute ammonia forming a negative sol that is not very stable.

<center>FORMATION</center>

Hydrolysis Methods

Gay-Lussac[65] boiled a concentrated solution of aluminum acetate and obtained a precipitate of hydrous alumina which redissolved when the temperature was lowered. Crum[66] heated a more dilute and more basic solution than Gay-Lussac's, first in a closed vessel and subsequently in an open one, to drive off the excess acetic acid. In this way a stable but opalescent colloidal solution was formed, containing alumina and acetic acid in the ratio of 5.5 : 1. The conditions of formation, namely prolonged digestion at high temperature with subsequent boiling in a medium having a slight solvent action, were conducive to the formation of relatively large, dense, non-reactive, primary particles. Accordingly, the oxide thrown down from the sol by electrolytes was an aged coagulum made up of crystalline particles that were not very soluble in acids or alkalis and had no mordanting action.

Graham[67] prepared a sol having properties similar to Crum's by heating an acetate solution for several days and then dialyzing in the cold. The time required for making Crum's sol may be materially shortened by peptizing freshly precipitated hydrous alumina with the smallest possible amount of acetic acid, diluting, and boiling to remove

[63] Renz: Ber., **36**, 2751 (1903); Archibald and Habasian: Trans. Roy. Soc., Canada, **10**, 69 (1916); Jander and Weber: Z. anorg. Chem., **131**, 266 (1923).

[64] Ber., **57B**, 808 (1924).

[65] Ann. chim. phys., **74**, 193 (1810).

[66] Ann., **89**, 168 (1854).

[67] Phil. Mag. (4) **23**, 290 (1862); *see, also*, Schlumberger: Bull. soc. chim. (3) **13**, 62 (1895).

the excess acid.[68]   Minachi and Okazaka[69] diluted a saturated solution of aluminum acetate in dilute acetic acid, added hydrogen peroxide, and dialyzed at 50 to 80°.   Krause and Wendt[70] obtained a sol by allowing water to act on the etherate of triethyl aluminum, $4(C_2H_5)_3Al \cdot 3(C_2H_5)_2O$.   Attempts to prepare colloidal alumina by dialysis of the chloride and nitrate[71] in the cold have not proved successful, owing to the relatively low degree of hydrolysis' of even 0.001 M solutions.[72]   Since the temperature coefficient of the hydrolysis of aluminum chloride is quite high,[73] Neidle[74] was able to get a 9.5% conversion of a 0.05 M solution of the salt by dialyzing for 37 hours at 75 to 80°.

Peptization Methods

Peptization by Salts and Acids.   Graham[75] peptized freshly prepared and thoroughly washed hydrous alumina in a solution of aluminum chloride and then dialyzed out the excess of the peptizing agent in the cold.   By this method a positively charged sol results that is very sensitive to the action of electrolytes.   The precipitate formed on coagulation is highly gelatinous, is readily soluble in acids and alkalis, and is a mordant.   The sol, therefore, bears the same relation to Crum's alumina sol that Graham's ferric oxide sol bears to the Péan de St. Gilles sol.   Analogous to ferric oxide sols, the difference in properties of the two colloidal aluminas is closely associated with the size and physical character of the hydrous particles.   Peptization of highly gelatinous alumina in the cold favors the formation of small, highly hydrous, primary particles that are more reactive and have a higher adsorption capacity than the more granular and denser particles formed during prolonged boiling in a medium possessing a slight solvent action.

The peptization of alumina gel by aluminum chloride does not take place very readily; but Hantzsch and Desch[76] got around this difficulty by adding ammonia to an aluminum chloride solution until the precipitate first formed failed to dissolve, and then dialyzing the sol.

[68] Weiser: J. Phys. Chem., **24**, 525 (1920).

[69] Japanese Pat. 41,726 (1922).

[70] Ber., **56B**, 466 (1923).

[71] Biltz: Ber., **35**, 4432 (1902).

[72] Ley: Z. physik. Chem., **30**, 219 (1899).

[73] Bjerrum: Z. physik. Chem., **59**, 343 (1907).

[74] Neidle and Barab: J. Am. Chem. Soc., **39**, 71 (1917).

[75] Ann., **121**, 41 (1862).

[76] Ann., **323**, 30 (1902); *cf.* Neidle and Barab: J. Am. Chem. Soc., **39**, 80 (1917).

By evaporating the transparent purified sol on the water bath, a glassy mass was obtained which was readily repeptized by water; but the new sol was quite opalescent owing to the formation of larger crystalline[77] particles during the process of evaporation. The sol prepared by hot dialysis was also slightly opalescent, possessing properties intermediate between Graham's and Crum's sols.

Highly purified sols cannot be prepared by adding ammonia to aluminum sulfate and dialyzing, because of the precipitating action of sulfate ion. However, one may add sodium carbonate and aluminum sulfate in the approximate ratio of 3 : 5 without any precipitation taking place; when the ratio is 7.5 : 5, half the alumina is thrown down; and when it is 12 : 5, all the alumina precipitates.[78]

Schneider[79] first peptized gelatinous alumina with a dilute solution of hydrochloric acid. The excess acid was removed by evaporating to dryness and repeptizing with water. The sol gave no test for chloride ion with silver nitrate in the cold, but silver chloride precipitated out on heating; with silver oxide, both silver chloride and the sol were thrown down. The failure to get a test for chloride ion in the cold was doubtless due to inhibition of the growth of silver chloride particles by the protecting power of hydrous alumina. Heating caused the silver chloride to show up, owing to partial agglomeration of the particles. The addition of silver oxide introduced the strongly adsorbed hydroxyl ion which neutralized the charge on the particles, precipitating the colloidal oxide together with silver chloride. Müller[80] boiled freshly prepared hydrous alumina with $N/20$ HCl and found the amount of acid required for complete peptization to be $1/72$ of that necessary to form aluminum chloride; Pauli[81] used $1/9$ of the theoretical amount; Davis, [82] $1/8$; and Kohlschütter[83] showed that the quantity of acid required was determined by the history of the sample. The dissolution of hydrous alumina in hydrochloric acid is always preceded by sol formation; the same may be true for sulfuric acid since Davis[82] found that 5.2 equivalents of the acid will peptize one mol of hydrous alumina.

Hydrous alumina is peptized by ferric chloride or nitrate but not

[77] Böhm and Niclassen: Z. anorg. Chem., **132**, 1 (1924).

[78] Mills and Barr: J. Chem. Soc., **41**, 341 (1882).

[79] Ann., **257**, 359 (1890).

[80] Z. anorg. Chem., **57**, 311 (1908); Sugden and Williams: J. Chem. Soc., 2426 (1926); *cf.* Schlumberger; Bull. soc. chim. (3) **13**, 60 (1895).

[81] Adolf and Pauli: Kolloid-Z., **29**, 281 (1921).

[82] J. Phys. Chem., **36**, 949 (1932).

[83] Kohlschütter and Neuenschwander: Z. Elektrochem., **29**, 253 (1923).

by ferric sulfate. The peptizing action of the chloride and nitrate is due to strong adsorption of ferric ions and of hydrogen ions resulting from hydrolysis of the salts. Such sols contain both hydrous alumina and hydrous ferric oxide. With ferric sulfate, the peptizing action of the cations is neutralized by strong adsorption of sulfate ion and no sol is formed. The order of peptizing power of different acids and salts on an aged gel thrown down from a boiling solution is:

$$HNO_3 > HCl > FeCl_3 > AlCl_3 > HC_2H_3O_2.[84]$$
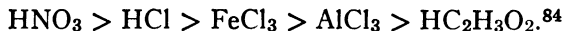
If we assume, as Lottermoser does, that a peptizer must contain one of the ions of the disperse phase, then the first step in the peptization of alumina by an acid or salt would be interaction, with the formation of some aluminum ion. This would seem to be an unnecessary step in view of the stronger peptizing action of hydrogen ion than of aluminum ion. On account of the relatively small ionization of acetic acid, its peptizing power is less than that of hydrochloric acid or nitric acid. However, the peptizing action of acetic acid is proportionately much greater than would be predicted from its relative strength. This is probably due both to peptization of alumina by acetic acid molecules and to an increased dissociation of the acid as alumina adsorbs hydrogen ions.[82] Bentley and Rose[85] reported many anomalies in the behavior of the sol formed by peptizing alumina with acetic acid; but for the most part, these appear to be the result either of experimental error or of misinterpretation of data.[86]

Thomas and Vartanian[84] give the following order of peptizing power of acids for alumina prepared by the action of hot water on amalgamated aluminum: trichloracetic > dichloracetic > nitric > hydrobromic > hydrochloric > monochloracetic > formic > glycolic > acetic > oxalic > tartaric > sulfuric. It is pointed out that this order of acids is inversely as the tendency (1) of their corresponding neutral salts to raise the pH value of aluminum "oxychloride" hydrosols and (2) for their anions to become coördinatively bound in complexes of the Werner type. From this it is deduced that the alumina sols are Werner complexes and that acids with anions having a strong tendency to bind coördinatively to the central metallic atom are poor colloidal peptizers whereas acids with a weak tendency to bind coördinatively are good peptizers (cf. p. 110). Stated in terms

[84] Weiser: J. Phys. Chem., 24, 521 (1920); cf. Ostwald and Schmidt: Kolloid-Z., 43, 276 (1927); Thomas and Vartanian: J. Am. Chem. Soc., 57, 4 (1935).
[85] J. Am. Chem. Soc., 35, 1490 (1913); Rose: Kolloid-Z., 15, 1 (1914).
[86] Weiser: J. Phys. Chem., 24, 522, 527 (1920).

of the adsorption theory of peptization, those acids whose anions are least strongly adsorbed are the best peptizers for hydrous alumina as a positive sol.

A very satisfactory sol is obtained by allowing aluminum amalgam to act on water containing a small amount of aluminum chloride.[87] Sheets of aluminum, 10 × 20 cm, were burnished to remove the film of oxide, and were placed in dilute hydrochloric acid until the surface was thoroughly cleaned. After rinsing, they were placed in mercuric chloride solution for one minute, taken out and washed thoroughly to remove the loose film of mercury, and each one placed in 1 l of approximately 0.015 N $AlCl_3$ which was stirred continuously with a mechanical stirrer. The action, which was rapid at the start, slowed down in a few hours, and the metal was re-treated as before. The process was continued until a sol of the desired composition was obtained or until no more of the "grown" alumina was peptized, in the presence of a large excess of the oxide, because of adsorption of all the peptizing aluminum ion.[87]

A sol results also by incomplete precipitation of the chloride ion of an aluminum chloride solution with silver oxide, followed by centrifuging out the resulting silver chloride.[88]

Removal of Agglomerating Electrolytes. Long-continued washing of alumina gel precipitated in the cold gives a fairly stable opalescent sol. The washing is accomplished more rapidly by the aid of the centrifuge or the supercentrifuge. Using the latter apparatus, Bradfield[89] threw out the particles of different sizes in different zones on the walls of the centrifuge vessel, and by repeptizing the different zones separately he obtained more or less uniform sols of graded particle size. The original precipitate may be obtained from either aluminum chloride or aluminum sulfate, but the gel from the latter is much more difficult to peptize by washing because of much stronger adsorption of sulfate than of chloride ion.

Tartar and Damerell[90] washed by decantation for several weeks without the centrifuge, the gel thrown down from cold sulfate, nitrate, and chloride solutions, first with dilute ammonia to remove the anions and finally with water to remove the ammonia. The resulting sols were very pure, the dispsersed phase being largely α-$Al_2O_3 \cdot 3H_2O$.

[87] Weiser: J. Phys. Chem., **35**, 1368 (1931); *cf.* Pauli and Schmidt: Z. physik. Chem., **129**, 202 (1927); Muttoné and Pauli: Kolloid-Z., **57**, 312 (1931); Thomas and Tai: J. Am. Chem. Soc., **54**, 841 (1932).

[88] Valko and Weingarten: Kolloid-Z., **48**, 10 (1929).

[89] J. Am. Chem. Soc., **44**, 969 (1922).

[90] J. Phys. Chem., **36**, 1419 (1932).

CONSTITUTION

Alumina sols like those of ferric oxide are regarded by some investigators as dispersions of basic salts. Thus Pauli,[91] as a result of physical-chemical observations similar to those on ferric oxide sol, concludes that the composition of the particles may be formulated: $[m\text{Al}(\text{OH})_3 \cdot n\text{AlOCl} \cdot \text{AlO}]^+$, Cl^-. There is no direct evidence of the existence of a basic chloride of the composition AlOCl, and the chances of its being in an aluminum sol are remote. Moreover, from measurements of the activities of the hydrogen and chloride ions, cataphoretic velocities, and equivalent conductivities, Mukherjee[92] demonstrated conclusively that alumina sols do not behave like ordinary electrolytes. For example, the activity and conductivity measurements on the sol cannot be reconciled with the behavior of electrolytes; and neither the cataphoretic velocity nor the equivalent conductivity of the sol increases regularly with the dilution as one would expect if the sol was behaving like an electrolyte (p. 57).

Thomas[93] suggests that the dispersed phase of alumina and chromic oxide sols formed by peptization of the gel with hydrochloric acid consists of olated and possibly oxolated aluminum oxychloride complexes of the Werner type resembling the poly-ol basic chromic salts formulated by Bjerrum. This assumption was made to account for the observation that the pH value of the sol is raised by the stepwise addition of approximately neutral electrolytes, the anion order being: oxalate > acetate > sulfate > halides > nitrate. The increased pH value was attributed to replacement of OH groups by the anion of the added salt, followed by the union of the displaced OH radicals with hydrogen ion to form water. The decrease in the pH value of alumina sols on heating, and the failure of the sols to return to the original value on cooling, were explained by assuming that the aquo groups in the complex radical give up hydrogen ions leaving hydroxo groups which then become "olated" forming larger aggregates.

The above explanation of the behavior of sols on adding electrolytes fails to take into account the displacement of radicals such as chloride and the changes in adsorption equilibria, involving both

[91] Adolf and Pauli: Kolloid-Z., **29**, 281 (1921); Pauli and Valko: Z. physik. Chem., **121**, 164 (1926); Pauli and Schmidt: **129**, 199 (1927); *cf.* Wintgen and Kühn: **A138**, 148 (1928).

[92] Kolloid-Z., **63**, 36; **65**, 72 (1933).

[93] Thomas and Whitehead: J. Phys. Chem., **35**, 27 (1931); Thomas and Tai: J. Am. Chem. Soc., **54**, 841 (1932); Thomas and von Wicklen: **56**, 794; Whitehead and Clay: 1844 (1934).

hydrogen and chloride ions, which accompany the agglomeration of the particles into larger aggregates as the charge is lowered. Moreover, the probability was overlooked[94] that the irreversible increase in pH value of the sols on aging in the cold is due to interaction of the gel with the acid. Prolonged heating decreases the pH value both by increasing the hydrolysis and cutting down the absorption of hydrogen ion. The process is irreversible because of the low solubility of the aged oxide.

The assumption that the alumina sols are basic salts or Werner complexes is not supported by x-ray analysis. Thus, the particles in the sol formed by hydrolysis of aluminum acetate are essentially γ-$Al_2O_3 \cdot H_2O$ or böhmite.[95] Similarly, the particles in the sol formed by adding ammonia short of precipitation to aluminum chloride solution followed by dialysis give the x-ray pattern for γ-$Al_2O_3 \cdot H_2O$.[96] There is little doubt but that the particles are hydrous γ-$Al_2O_3 \cdot H_2O$ in sols formed by peptizing alumina gel with dilute hydrochloric acid at 70°. It is altogether likely that the dispersed phase is hydrous γ-$Al_2O_3 \cdot H_2O$ in all alumina sols when first prepared by the ordinary methods. An aged sol may contain more or less α-$Al_2O_3 \cdot 3H_2O$ or γ-$Al_2O_3 \cdot 3H_2O$, the latter being the stable form of hydrated alumina at ordinary temperatures (p. 90).

The constitution of the sols would therefore seem to be relatively simple. They consist essentially of a hydrous alumina hydrate with adsorbed aluminum chloride, hydrochloric acid, aluminum, hydrogen, and chloride ions. Analogous to the corresponding ferric oxide sols the constitution of the particles may be represented diagrammatically as shown in Fig. 22a, page 117. This indicates that the hydrous γ-$Al_2O_3 \cdot H_2O$ adsorbs chloride which is not readily displaced by coagulating electrolytes; and that the stabilizing ion is chiefly aluminum rather than hydrogen ion. This concept of the constitution of the particle may be formulated:

$$[xAl_2O_3 \cdot (x + y)H_2O \cdot zHCl]Al_n \cdot (3n - q)Cl, qCl.$$

PROPERTIES

General Properties

Sols formed by the hydrolysis of aluminum acetate solution (Crum) are not spherical but are anisotropic, as evidenced (1) by sparkling of the sol in the ultramicroscope,[97] (2) by showing a clearly

[94] *Cf.* Weiser: J. Phys. Chem., **35**, 1368 (1931); Tartar, Bryan, and Shinn: J. Am. Chem. Soc., **55**, 2266 (1933).

[95] Böhm: Z. anorg. Chem., **149**, 208 (1925); Böhm and Niclassen: **132**, 1 (1924)

[96] Fricke and Havestadt: Z. anorg. Chem., **196**, 123 (1931).

[97] Szegvari: Z. physik. Chem., **112**, 315 (1924).

defined streaming double refraction[98] (p. 291), and (3) by the depolarization of the Tyndall light.[99]   On the other hand, sols formed by peptization methods behave optically as if the particles are spherical.[100]

The relative viscosity of a sol prepared by Crum's method is a simple linear function of the concentration.[101]   The viscosity changes but slightly with increasing pH value until between $pH = 7$-8, when there is a sudden increase to a maximum followed by a decrease to a constant value.   The abrupt increase at about $pH = 7$ is probably due to rapid agglomeration of the particles into a kind of network that offers resistance to flow.   This is followed by partial coalescence which releases some adsorbed water and thus lowers the viscosity to a certain extent.   The stepwise addition of electrolytes causes the viscosity to decrease slightly at first and then to rise.   This behavior is similar to that observed with ferric oxide sol and for the same reason (p. 66).   With increasing "colloid-equivalent" of the sol (p. 57) the viscosity decreases to a minimum and then increases slightly.[102]

The change in the viscosity of a sol on adding electrolytes serves as a useful method for following the course of the coagulation process and for estimating the precipitation values of electrolytes.[103]

The dielectric constant of sols formed both by Crum's method and by dialyzing aluminum chloride partly neutralized with ammonia, is greater than that of water.   The addition of small amounts of electrolytes causes a decrease in the dielectric constant which is probably due to an increase in the hydration of the particles.   There is no observable change in the dielectric constant when a thixotropic sol sets to a jelly.[104]

Coagulation by Electrolytes

Adsorption of Precipitating Ions.   The precipitation values of several electrolytes for Crum's colloidal alumina, and the adsorption of the anions in the neighborhood of the precipitation concentration,

[98] Aschenbrenner: Z. physik. Chem., **127**, 415 (1927).

[99] Lange: Z. physik. Chem., **A132**, 19 (1928).

[100] Diesselhörst and Freundlich: Physik. Z., **17**, 124 (1916).

[101] Gann: Kolloid-Beihefte, **8**, 73 (1916).

[102] Muttoné and Pauli: Kolloid-Z., **57**, 319 (1931).

[103] Freundlich and Ishizaka: Kolloid-Z., **12**, 232 (1913); Gann: Kolloid-Beihefte, **8**, 73 (1916).

[104] Kistler: J. Phys. Chem., **35**, 815 (1931); Fricke and Havestadt: Z. anorg. Chem., **188**, 390 (1930); **196**, 123 (1931); Fricke: Kolloid-Z., **56**, 168 (1931).

are given in Table VII. The first part of the table is taken from the work of Gann,[105] and the last part from observations in the author's[39] laboratory.

TABLE VII

ADSORPTION DURING COAGULATION OF COLLOIDAL ALUMINA

Ions	Precipitation value millimols/l	Adsorption value	
		Millimols/g	Milliequivalents/g
Ferrocyanide..........	0.08	0.073	0.29
Ferricyanide..........	0 10	0.09	0.27
Oxalate..............	0.36	0.18	0.36
Picrate..............	4.00	0.18	0.18
Salicylate............	8.00	0.30	0.30
Ferrocyanide..........	0.094	0.320	1.280
Ferricyanide..........	0.133	0.405	1.214
Sulfate..............	0.269	0.498	0.997
Oxalate..............	0 350	0.571	1.142
Chromate............	0.650	0.435	0.870
Dithionate	0.813	0.328	0.657
Dichromate..........	0.888	0.318	0.629

In accord with the usual behavior, the ion with the highest valence precipitates at the lowest concentration, but ions of the same valence show considerable variation in precipitating power. The adsorption values of precipitating ions during the coagulation process show considerable variation from equivalence. There are two reasons for this: first, since the ions of higher valence are adsorbed more strongly than ions of lower valence, less of the former need be adsorbed in order to lower the potential to the coagulation value; and second, adsorption continues after the potential is lowered to the point of coagulation. The extent of the adsorption by the agglomerating particles varies but, in general, is greater the higher the valence of the precipitating ion. In accord with what one would expect, the most strongly adsorbed ion has the highest precipitating power (lowest precipitation value) as shown by the data in the second part of Table VII.

[105] Kolloid-Beihefte, 8, 66 (1916); cf. Ishizaka: Z. physik. Chem., 83, 108 (1913); Balarew and St. Krastew: Kolloid-Z., 51, 329 (1930).

Displacement of Chloride.   The displacement of chloride during the coagulation of alumina sols by electrolytes[106] has been followed potentiometrically, using the procedure previously described (p. 73). At the same time the change in the pH value of the sol was determined, using a specially designed hydrogen electrode.
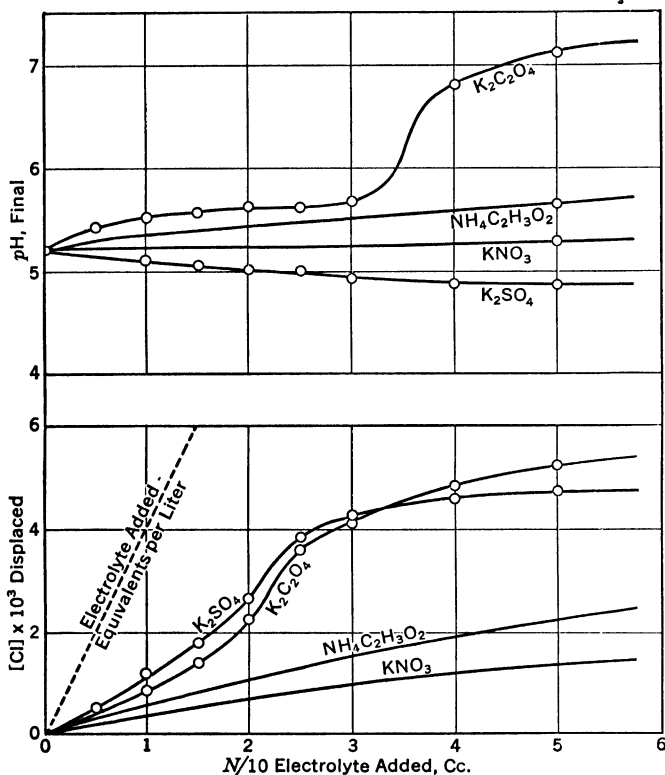
FIG. 20.—Curves showing (1) change in pH value and (2) displacement of chloride, on titrating alumina sol with several electrolytes.

Two sols were used: the first prepared by peptization of "nascent" fibrous alumina in aluminum chloride (p. 109), and the second by adding ammonia to aluminum chloride short of precipitation and dialyzing in the hot.   Some observations with the latter type of sol are shown graphically in Fig. 20.   The curve for displacement by citrate follows about the same course as that for displacement by sul-

[106] Weiser: J. Phys. Chem., **35**, 1368 (1931).

fate although the precipitation value of citrate is somewhat lower. If the citrate solution contained largely trivalent ions, the first part of the curve with this salt would be appreciably higher than that of the same normal concentration of divalent ions. The order of chloride-displacing power below the precipitation concentration for the sol is: citrate > sulfate > oxalate > acetate > nitrate. Above the precipitation value where the supernatant oxalate solution becomes less acid, oxalate and sulfate exchange places. This is because the oxalate solution contains relatively more of univalent bioxalate ion in the more acid range and relatively more of the strongly adsorbed bivalent oxalate ion in the less acid range beyond the precipitation value. The displacement curve with oxalate never rises above that for sulfate when more acid is used.

The order of precipitating power of the several salts is: citrate > sulfate > oxalate > acetate > nitrate. This order is identical with the order of chloride-displacing power.

A comparison of the pH value and chloride-displacement curves on adding the several electrolytes to alumina sols reveals a distinct difference in the order. Thus the order in which the alkali salts increase the pH value of the several sols is: citrate > oxalate > acetate > nitrate > sulfate. It will be noted that the addition of sulfate actually raises slightly the pH value of the sol under consideration and that nitrate has but little effect. As would be expected, the most marked tendency to raise the pH value of acid sols is manifested by the electrolytes with a buffering action by virtue of their alkali reserve. It should be pointed out that it is not strictly accurate to compare the pH value curves in the region just above and below the precipitation concentration of salts having multivalent anions, with the curves for the same equivalent concentration of the salts of univalent ions, since such concentrations of the latter salts affect the stability of the sol much less than the former and so influence the adsorption equilibria to a much smaller extent. The order at the precipitation concentration is: acetate > citrate, oxalate > nitrate > sulfate.

Some observations of the simultaneous displacement of chloride and adsorption of sulfate[107] are shown graphically in Fig. 21. The adsorption curve follows an unbroken course throughout the entire concentration range, but there is a slight bend just above the precipitation value corresponding to a similar bend in the chloride displacement curve. The sulfate adsorption is appreciably greater than the

[107] Weiser and Gray: J. Phys. Chem., **36**, 2178 (1932).

amount of chloride displaced since a part of the sulfate taken up corresponds to chloride measurable potentiometrically in the intermicellar solution. Contrary to observations of Peterson and Storks[108] on the adsorption of chromate by hydrous alumina both above and below the precipitation value, the sulfate adsorption follows a smooth course
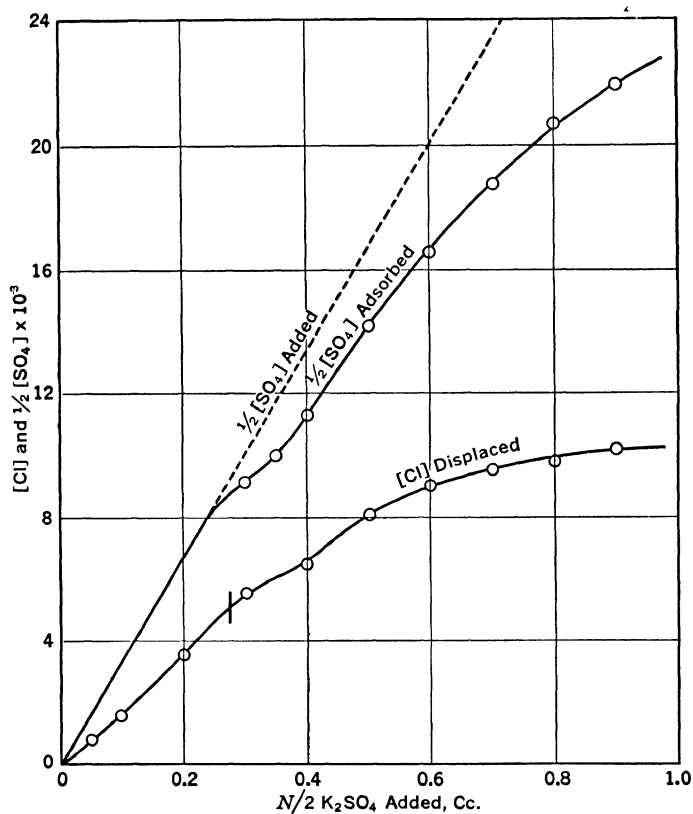
FIG. 21.—Simultaneous displacement of chloride and adsorption of sulfate on titrating alumina sol with K_2SO_4.

above that of the chloride-displacement curve throughout the entire concentration range. A marked break in the adsorption curve obtained by Peterson and Storks is probably due to a displacement of the adsorption equilibrium by ultrafiltration (p. 58).

[108] J. Phys. Chem., **35**, 649 (1931); *cf., also,* Peterson and Trimble: Proc. Iowa Acad. Sci., **38**, 165 (1931).

As with ferric oxide sol, we may represent diagrammatically the constitution of the micelle before and after the addition of electrolyte, by Fig. 22a and b, respectively. As the diagram indicates, the lowering of the ζ-potential on the particles following the addition of small amounts of multivalent ions is due to the much stronger adsorption of multivalent ions than that of univalent chloride. The result is that the adsorbed ions are drawn closer to the inner layer, as indicated
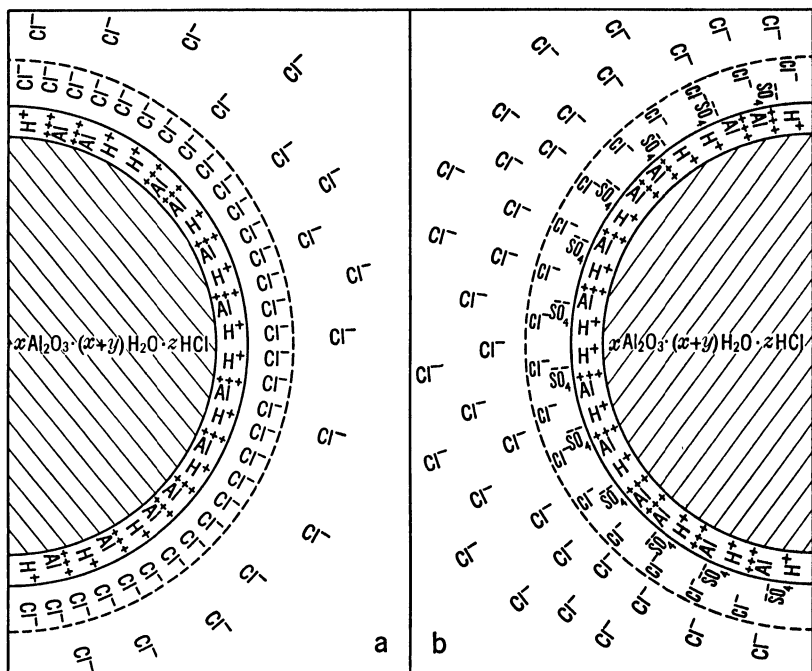
FIG. 22.—Diagrammatic representation of the constitution of a particle of colloidal alumina (a) before and (b) after the addition of potassium sulfate.

in the diagram, thus reducing the thickness of the double layer. Since the potential difference between two layers of opposite sign with constant charge density is directly proportional to the distance between them, it necessarily follows that the thinner layer will have a lower potential. If the adsorbability of ions is determined by valency alone, multivalent ions will have a stronger discharging action than univalent ions because the larger charge on the former will cause them to be attracted more closely to the inner layer with the consequent lowering of potential. As is well known, a similar discharging action with uni-

valent precipitating ions takes place only at relatively high concentrations.

The lowering of the potential on the particles results in coalescence and agglomeration of the particles with a consequent decrease in specific surface. This manifests itself in an increase in the amount of chloride displaced for a given increment in the multivalent ion added as the region of rapid coagulation is approached. Hence the upward bend in the chloride-displacement curve with multivalent ions, becomes more marked in the region of rapid coagulation. Above the coagulation point, the chloride is displaced from the precipitate by exchange adsorption without any marked decrease in specific surface, and the curve follows the usual course of the adsorption isotherm. This combination of conditions accounts for the S-shape of the chloride-displacement curve with all electrolytes having a high precipitating power and causing coagulation above a critical concentration.

Electrolytes with relatively low precipitating power, which do not cause rapid coagulation in a critical zone, give chloride displacement curves which follow throughout the course of the adsorption isotherm as a result of exchange adsorption and gradual agglomeration.

The adsorption of the added anions by the colloidal particles will tend to increase the adsorption of cations, and the agglomeration with decrease in specific surface which accompanies the lowering of the charge will tend to decrease the adsorption of both cations and anions. In the sols under observation, the adsorbed hydrogen ion is in equilibrium with hydrogen ion concentrations between 10^{-4} and 10^{-5} mol per liter. The shifting of the adsorption equilibria which accompanies the addition to the sol of a salt of a strong acid and a strong base will increase slightly, decrease slightly, or leave unchanged the pH value, depending, in any given case, on the relative magnitude of the two opposing tendencies above mentioned. With salts such as potassium citrate and ammonium acetate buffer action always renders the pH value of the sol-electrolyte mixtures higher than that of the sol alone.

In the light of the evidence from x-ray diffraction studies and from the above experimental procedures, not much appears to be gained by assuming that an alumina sol is an indefinite complex poly-ol basic aluminum salt of the Werner type and that the increase in pH value on adding such salts as potassium nitrate and potassium sulfate to the sol is due to displacement of OH groups which unite with H^+ to form water (p. 110). Indeed, as we have seen, the addition of

potassium sulfate to one such sol caused the pH value to decrease slightly.

Velocity of Coagulation. The velocity of slow coagulation (*cf.* Vol I, p. 89) may be followed from the change in viscosity during the process. This has been done in Freundlich's laboratory by Gann,[109] who showed that the process is autocatalytically accelerated, taking place in accordance with the equation $\dfrac{dx}{dt} = k(1 + b_1 x)(1 - x)$, where x is the increase in viscosity after time t expressed as a fraction of the total increase; and k and b_1 are constants. For concentrated sols the coagulation process is more nearly represented by the equation $\dfrac{dx}{dt} = k_1(1 - x)^2$. The coefficient k_1 increases rapidly with the concentration of the electrolyte during slow coagulation, whereas for very rapid coagulation the velocity is independent of the nature of the electrolyte. Smoluchowski[110] assumes that, in rapid coagulation, all the collisions of particles are inelastic because of the great attractive forces existing between particles; and in slow coagulation, only a portion of the collisions result in immediate union, because the mutual attraction is not always great enough to overcome the repulsive effect of more highly charged particles. Freundlich turns this around and assumes a constant force of attraction for a given concentration of electrolyte below that necessary for rapid coagulation; but because of repulsion between charged particles, only those collisions are inelastic in which the particles collide with sufficient force. Obviously, the greater the charge on the particles, the greater must be the velocity of collision in order to overcome the repulsive effect and so to bring about coalescence and agglomeration. The rapid increase in the velocity of slow coagulation is due to the proportionately larger number of inelastic collisions that result when the charge on the particles is reduced by adsorption of precipitating ions.

The Sol-gel Transformation. The sol prepared by Crum's method is quite thixotropic. The addition of a suitably small amount of electrolyte causes it to set to a jelly which is converted to a sol by shaking and re-forms a jelly once more on standing. Unlike the sol of ferric oxide, which is thixotropic only when fairly concentrated, Crum's sol is thixotropic at concentrations as low as 1% Al_2O_3.[111]

[109] Kolloid-Beihefte, **8**, 125 (1916).

[110] Z. physik. Chem., **92**, 129 (1917); Kolloid-Z., **21**, 98 (1917).

[111] Freundlich and Bircumshaw: Kolloid-Z., **40**, 19 (1926); Freundlich: **46**, 294 (1928).

There is no connection between the thixotropic behavior and the anisotropic character of the sol as revealed by its streaming double refraction.

HYDROUS GALLIUM OXIDE

Gallium oxide requires a very slight hydroxyl ion concentration for its precipitation and is thrown down in a highly gelatinous form not only by both strong and weak alkalis but also by salts of weak acids,[112] such as carbonate, bicarbonate, sulfide, sulfite,[113] etc. Tartaric acid prevents the precipitation presumably because complex tartrates are formed.[114] The hydrous oxide behaves like an acid in the presence of both ammonia and alkalis forming gallates.[115] From the alkali solution the oxide precipitates very slowly out of contact with air, but it is readily thrown down by carbon dioxide as a flocculent mass entirely different from the granular crystals of $Al_2O_3 \cdot 3H_2O$ which precipitate from aluminate solution.[116] The precipitate ages fairly rapidly even at ordinary temperatures, as evidenced by a progressive loss of adsorbed water and a decrease in the solubility in alkalis. This aging progresses more rapidly in the presence of alkali.

The hydrous precipitate thrown down with ammonia contains less water than corresponds to $Ga_2O_3 \cdot 3H_2O$ or $Ga(OH)_3$ when dried in a vacuum desiccator over sulfuric acid. The water content of a preparation obtained from an old alkali solution and dried over sulfuric acid is greater than that for a trihydrate; but the more gelatinous precipitate from a newly formed alkali solution falls considerably below that for a trihydrate even when dried in the air at ordinary temperatures.[116]

Havestadt and Fricke[21] report that a gel thrown down from gallium chloride with ammonia gives no x-ray diffraction. On the other hand, the powdery precipitate formed by strongly diluting the solution of the ammonia precipitate in excess ammonia, gives a definite x-ray diffraction pattern entirely different from that of anhydrous Ga_2O_3. It is apparent, therefore, that the oxide forms a hydrate, but the composition has not been established with certainty. It is claimed that the composition is represented by the formula

[112] Lecoq de Boisbaudran: Chem. News, **35**, 148, 157, 167 (1877).

[113] Dennis and Bridgman: J. Am. Chem. Soc., **40**, 1531 (1918).

[114] Lecoq de Boisbaudran: Compt. rend., **93**, 294, 329, 815 (1881).

[115] Fricke and Blencke: Z. anorg. Chem., **143**, 183 (1925); Fricke and Meyring: **176**, 325 (1928).

[116] Fricke: Z. Elektrochem., **30**, 393 (1924).

$3Ga_2O_3 \cdot 5H_2O$ both when dried at $100°$ and when dried over phosphorus pentoxide at room temperature. These observations should be confirmed and extended by running the complete dehydration isobar.

Owing to the gelatinous nature of the precipitate with ammonia, one might expect sol formation to result from thorough washing of the gel. Moreover, it is not unlikely that a small amount of gallic chloride or hydrochloric acid would peptize the gel, forming a positive sol, or a slight excess of alkali, a negative sol; but there is no record of such experiments having been performed. There is some evidence that a part, at least, of the hydrous oxide is in the sol form in the presence of excess alkali. Thus, by conducting carbon dioxide into an alkali solution newly formed in the cold, one obtains a very voluminous gel, quite different in appearance and properties from the flocculent precipitate thrown down from an old alkali solution.

HYDROUS INDIUM OXIDE

Indium oxide, In_2O_3, in a highly gelatinous form is precipitated by adding alkali, ammonia, hydroxylamine,[117] or dimethylamine[118] to a solution of an indium salt. If the gel is digested on the water bath it is transformed to a granular material.[119] The precipitated oxide loses water continuously on heating, and there is no indication of the existence of a hydrate.[120] The last traces of the adsorbed water are not removed until a temperature of $650°$ is reached; but the oxide undergoes no appreciable decomposition below $850°$.[121] Like hydrous gallia and alumina, the precipitate ages slowly at ordinary temperature but rapidly at the boiling point, particularly in the presence of alkali. The newly formed oxide dissolves in the cold in excess alkali but soon precipitates in a much less reactive form.[122] This precipitation is almost quantitative in the hot.[123] Unfortunately we do not know whether in the cold the oxide is dissolved by excess alkali forming an indate, or whether it is peptized forming a negative sol, or whether both processes occur simultaneously. Nor do we know whether the precipitate which comes down on

[117] Dennis and Geer: Ber. **37**, 961 (1904).
[118] Renz: Ber., **34**, 2763 (1901); **36**, 1847, 2751, 4394 (1903); **37**, 2111 (1904).
[119] Thiel and Luckmann: Z. anorg. Chem., **172**, 353 (1928).
[120] Carnelley and Walker: J. Chem. Soc., **53**, 88 (1888).
[121] Thiel and Koeltsch: Z. anorg. Chem., **66**, 288 (1910).
[122] Meyer: Ann., **150**, 137 (1869).
[123] Richards and Boyer: J. Am. Chem. Soc., **41**, 133 (1919).

standing is an aged hydrous oxide as with chromic oxide or a definite hydrate as with alumina. These problems should be investigated.

As ordinarily prepared, hydrous indium oxide is but slightly soluble in ammonia. Renz[124] claimed at one time to have obtained an ammonia-soluble form of the gel, but later he was not sure about it. It is, of course, altogether possible that the hydrous oxide may be thrown down under special conditions in a more soluble or more readily peptizable form than that ordinarily obtained; if so, there should be little difficulty in determining whether a sol is formed, as has been suspected.[125]

Whatever may be the nature of the alkali solution of hydrous indium oxide, the gel is readily converted into a sol by thorough washing with distilled water. Even the denser gel thrown down at 100° is peptized in this way. The colloidal solutions obtained by Thiel precipitated out in a few weeks' time; but there is no doubt that very stable sols could be formed by supercentrifugal washing. To prevent sol formation during quantitative washing, it is only necessary to follow the time-honored practice of adding a little ammonium salt to the wash water.

A stable colloid is easily obtained by passing air through a cold solution of indium monoiodide.[126] The reaction

$$2InI + xH_2O + O_2 = In_2O_3 \cdot xH_2O + 2HI$$

goes slowly, practically all the oxide remaining colloidally dissolved. If desired, there seems no reason why this sol should not be purified by dialysis.

By carrying out the oxidation of indium monoiodide in the hot, 99% of the indium is converted into hydrous oxide, most of which precipitates out. Obviously, the oxide ages quite rapidly, or it would not precipitate from dilute acid solution in which the newly formed gel is very soluble. Indeed, the oxide thrown down in this way is almost insoluble in the cold in dilute acids and dissolves but slowly in concentrated ones, a behavior analogous to the aging of the better-known hydrous oxides of aluminum and chromium.

Anhydrous indium oxide likewise furnishes a good example of the influence of the physical character of an oxide on its chemical properties. Not only is an oxide heated to 850° acted on much more readily

[124] Ber., **36**, 1848, 2754 (1903).

[125] Thiel: Z. anorg. Chem., **40**, 322 (1904); cf., however, Thiel and Koeltsch: **66**, 300 (1910).

[126] Thiel and Koeltsch: Z. anorg. Chem., **66**, 300, 304 (1910).

than one ignited at $1200°$,[127] but a newly formed oxide decomposes into In_3O_4 and O_2 between 1200 and $1500°$ much more rapidly than a dense preparation aged by long ignition,[128] at a low red heat.

HYDROUS THALLIC OXIDE

The most hydrous form of thallic oxide is obtained by adding ammonia or alkali in slight excess to a thallic salt solution in the cold. It is also formed by the oxidation of TlOH with chlorine.[129] The very insoluble, voluminous precipitate is reddish brown in color like hydrous ferric oxide; it adsorbs alkali strongly, and in consequence ammonia is always used as the precipitant in the estimation of thallium as Tl_2O_3.[130] If the solution after precipitation is heated to boiling, the brown mass of hydrous oxide loses practically all its water, becoming a dark granular powder. The oxide precipitated in the cold and dried in the air has a composition approaching $Tl_2O_3 \cdot H_2O$;[131] it has, there-fore, been tacitly assumed that the red-brown slimy precipitate is a monohydrate. From the dehydration isobar, Hüttig and Mytyzek[129] showed that the oxide formed by oxidizing TlOH with chlorine con-tains no definite hydrate. Moreover the x-ray diffraction pattern from the hydrous precipitate was identical with that from anhydrous Tl_2O_3.

By treating an alkaline solution of a thallous salt with hydrogen peroxide at room temperature,[132] one obtains a dark-brown, flocculent precipitate of hydrous oxide which changes slowly to small lustrous crystals of almost anhydrous Tl_2O_3. If the reaction is carried out at 80 to $100°$, the oxide is a black, sandy powder. The density of the black oxide is 5.6% higher than that of the brown; and the brown dis-solves much more readily in acids and is more readily reduced to the thallous state by boiling water. It is probable that these differences in properties are due entirely to variations in the physical character of the mass, as determined by the conditions of formation, and not to allotropy, as assumed by Rabe.[133] Indeed, by heating the brown oxide to $500°$, the primary particles sinter together and assume per-manently the properties of black oxide.

[127] Renz: Ber., **36**, 1848 (1903); Thiel and Koeltsch: Z. anorg. Chem., **66**, 296 (1910).

[128] Thiel: Z. anorg. Chem., **40**, 322 (1904).

[129] Hüttig and Mytyzek: Z. anorg. Chem., **192**, 187 (1930).

[130] Meyer: Z. anorg. Chem., **24**, 364 (1900).

[131] Carnelley and Walker: J. Chem. Soc., **53**, 88 (1888).

[132] Rabe: Z. anorg. Chem., **48**, 427 (1906); **50**, 158 (1906).

[133] Z. anorg. Chem., **55**, 130 (1907).

A crystalline hydrate of thallic oxide, $Tl_2O_3 \cdot 3H_2O$ or $Tl(OH)_3$,[134] stable to a temperature of 340°, is said to be formed by prolonged fusion of Tl_2O_3 with KOH and subsequently treating the yellow mass with water. These observations should be repeated, as the formula was derived from thallium analyses the accuracy of which is not known.

Thallous oxide forms a definite crystalline hydrate, $Tl_2O \cdot H_2O$ or TlOH, soluble in water and possessing basic properties of the same order of magnitude as the caustic alkalis.

[134] Carnegie: Chem. News, 60, 113 (1889).

CHAPTER IV

HYDROUS CHROMIC OXIDE

Hydrous chromic oxide is the only oxide of chromium which will receive detailed consideration. So little authentic information is available concerning the so-called chromous hydroxide and chromo-chromic oxide[1] that a consideration of their colloidal properties must await further study.

CHROMIC OXIDE GEL

Formation and Composition

The addition of ammonia or an alkali to a solution of chromic salt precipitates chromic oxide as a highly hydrous gel, the composition and properties of which depend on the conditions of precipitation and the subsequent treatment. The gel is frequently called chromic hydroxide and assigned the formula $Cr(OH)_3$ or $Cr_2O_3 \cdot 3H_2O$ in spite of the fact that 50 years ago van Bemmelen[2] failed to find such a hydrate and that subsequent investigations confirm his results. For example, Simon, Fischer, and Schmidt[3] studied the isobaric dehydration of the oxide precipitated and aged under various conditions. A few of the isobars are shown in Fig. 23. Curve B is for a gel thrown down from chromic nitrate solution with ammonia at 60°. Similar smooth curves indicating the absence of hydrates were obtained with gels (1) thrown down from the chloride with ammonia, (2) formed by slow hydrolysis of chromic nitrate for 8 weeks in a dialyzer, (3) precipitated spontaneously from the sol which results on peptizing the freshly formed gel in alkali. Curve A is for a gel which was thrown down on reducing a solution of chromic acid with hydrazine hydrate, washed thoroughly by decantation, and dried in a vacuum desiccator

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[1] Moberg: J. prakt. Chem., **43**, 119 (1843); Péligot: Ann. chim. phys. (3) **12**, 544 (1844); Baugé: (7) **19**, 178 (1900).

[2] Rec. trav. chim., **7**, 37 (1888); cf. von Baikow: J. Russ. Phys.-Chem. Soc., **39**, 660 (1907).

[3] Z. anorg. Chem., **185**, 107 (1930); cf., also, Hackspill and Kieffer: Ann. chim. (10) **14**, 227 (1930).

over sulfuric acid for 8 weeks. Unlike the curves obtained with other gels, this one can be drawn to give a very slight point of inflection in the neighborhood of $3H_2O : 1Cr_2O_3$. Simon draws the curve so that a similar slight inflection is indicated at $1H_2O$, but the data fail to justify this. Indeed, it is questionable whether the form of the curve in the neighborhood of $3H_2O$ indicates the presence of a trihydrate or whether it is the result of experimental error. Simon thinks the aging may have resulted in the formation of a hydrate in this case and not
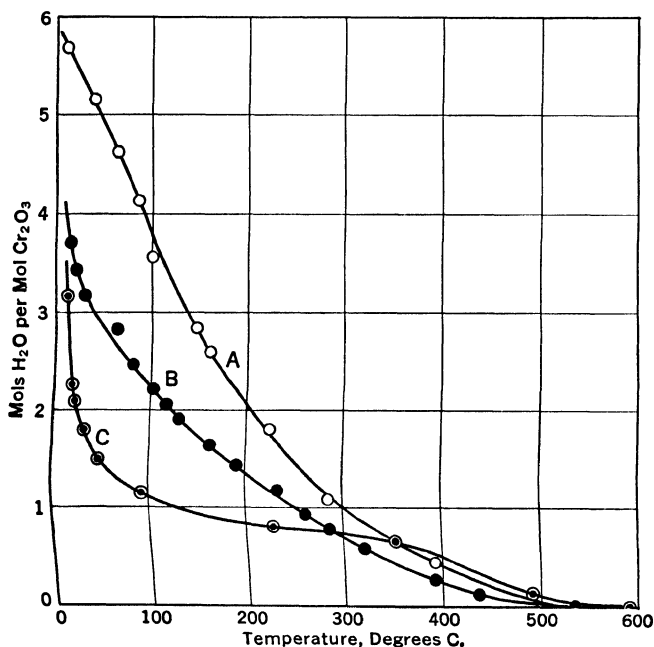
FIG. 23.—Dehydration isobars of hydrous chromic oxides (A and B) and of hydrous chromic oxide monohydrate (C).

in others because of the greater purity of the sample. It is a great pity that the experiment was not repeated by Simon on the same sample and on a second sample prepared in the same way. Anyone who has carried out dehydration experiments on irreversible systems like the one under consideration knows how easy it is to get erroneous data as the result of accidental temperature fluctuations, a slight leak in the apparatus, or the failure to attain an equilibrium state at each temperature. In this connection a paper by Hantzsch and Torke[4]

[4] Z. anorg. Chem., **209**, 60 (1932).

calls for special mention. These investigators measured the time of drying at each temperature in minutes, the times varying from 100 to 360 minutes. Since it is well known that days and even weeks at low temperatures are required to establish equilibrium, the broken dehydration curves obtained by Hantzsch and Torke are meaningless except as they furnish a good example of how poor technique may lead to erroneous conclusions.

The rate of dehydration of chromic oxide gel in the presence of various gases increases in the order: $NH_3 < CH_3OH < O_2 < H_2 < N_2$.[5]

Féreé[6] claims to have obtained the compound $Cr_2O_3 \cdot H_2O$, described as a brownish black amorphous powder, by electrolysis of a neutral solution of chromic chloride with a platinum cathode, but this has not been confirmed.[7] It is also claimed by some that a green hydrate, Guignet's green,[8] is formed by fusing one part of bichromate of sodium, potassium, or ammonium with three parts of boric acid, but there is a difference of opinion as to the formula.[9] Wöhler and Becker[10] obtained a pigment similar in color to Guignet's green by heating the ordinary oxide in an autoclave at 180–250°. The oxide was taken to be a definite hydrate since its composition on drying at 80° may be represented by the formula $2Cr_2O_3 \cdot 3H_2O$.

Simon, Fischer, and Schmidt[3] studied the isobaric dehydration of Guignet's green and showed that the water was given off continuously without any evidence of its being a hydrate. On the other hand, the oxide formed by heating the freshly formed gel in an autoclave for two weeks at 200° and 15 atmospheres gave an isobar which indicated the presence of a monohydrate; and a gel heated for 8 hours at 370–380° and 250 atmospheres was transferred completely into the monohydrate. The dehydration curve for the latter, C Fig. 23, shows isothermal decomposition of the hydrate at approximately 365°. The monohydrate[11] is formed also when a chromic nitrate-nitric acid solution is heated in an autoclave as described in the preparation of alumina monohydrate (p. 94).

[5] Hüttig and Strial: Z. anorg. Chem., **209**, 249 (1932).

[6] Bull. soc. chim. (3) **25**, 620 (1901); cf. Bunsen: Pogg. Ann., **91**, 619 (1854); Geuther: Ann., **118**, 66 (1861).

[7] Simon, Fischer, and Schmidt: Z. anorg. Chem., **185**, 107 (1930).

[8] Guignet: Jahresber., 761 (1859).

[9] Salvétat: Compt. rend., **48**, 295 (1859); Scheurer-Kestner: Dinglers polytech. J., **176**, 386 (1865); Eibner and Hue: Farben-Ztg., **15**, 2106, 2157, 2213, 2268, 2319 (1910).

[10] Z. angew. Chem., **21**, 1600 (1908); **24**, 484 (1911).

[11] Ipatiev and Muromzev: Ber., **60B**, 1980 (1927).

X-ray studies on hydrous chromic oxide throw no light on the composition of the gel. Thus the following gels gave no x-ray diffraction pattern:[12] (1) the fresh gel precipitated with ammonia; (2) No. (1) aged 305 days under water; (3) the gel precipitated from the sol in 11 N alkali during 35 days; and (4) No. (3) aged 305 days in contact with the alkali. On the other hand, the monohydrate formed under pressure gives a definite x-ray pattern differing from that of the anhydrous oxide.

PROPERTIES

Aging

Hydrous chromic oxide, freshly precipitated from a cold chromic salt solution with an alkali or ammonia, is readily soluble in acids, giving the corresponding salts, and is peptized by alkali hydroxides with the formation of a negative sol. On standing, the oxide undergoes a change in physical character accompanied by a marked decrease in solubility and reactivity. This "aging" process is probably due to the growth and agglomeration of primary colloidal particles, since the velocity of change increases rapidly with rising temperature and is hastened in a medium possessing a slight solvent action. Recoura[13] followed the change by determining the molar heat of solution in hydrochloric acid of the oxide precipitated with acid from the colloidal solution in alkali, after definite intervals of time. From his results given in Table VIII, it will be noted that the change in the heat of solution

TABLE VIII

MOLAR HEAT OF SOLUTION OF HYDROUS CHROMIC OXIDE PRECIPITATED
FROM SOLUTION IN ALKALI

Time	Molar heat of solution, calories	Time	Molar heat of solution, calories
0.................	20.70	7 hours...........	2.40
10 minutes..........	7.90	1 day.............	1.75
1 hour.............	5.80	7 days...........	1.20
2 hours............	3.90	30 days...........	0.75
4 hours............	2.85	60 days...........	0.50

[12] Fricke and Wever: Z. anorg. Chem., **136**, 322 (1924); cf., also, Simon, Fischer, and Schmidt: **185**, 107 (1930); Lottermoser and Lottermoser: Kolloid-Beihefte, **38**, 1 (1933).

[13] Compt. rend., **120**, 1335 (1895); cf. Fricke and Windhausen: Z. physik. Chem., **113**, 248 (1924); Z. anorg. Chem., **132**, 273 (1924).

is quite marked during the first few minutes.   This change is accompanied by a similar decrease in solubility.   Since the aging is more rapid at higher temperatures, the oxide precipitated at 100° is much less soluble than that thrown down at room temperature.

Solutions of hydrous chromic oxide in alkali were found by Bourion and Senechal[14] to lose their reducing power toward hydrogen peroxide on standing.   The reaction (loss of reducing power) with a solution containing 0.938 g Cr_2O_3 and 58 g NaOH per l appeared to be approximately tetramolecular for the first 8 hours.   The results were attributed to the transformation of the original oxide into complexes of decreasing chemical activity, the tetramolecular order being only apparent.   Bourion and Senechal evidently believe that hydrous chromic oxide dissolves in alkali with the formation of chromite; but in reality it is held in colloidal solution for the most part.   The decreased activity on standing is due to a gradual change in the physical character of the particles, a change that is sufficiently marked with a concentrated sol to cause partial precipitation in a short time. This transformation from a very soluble to a less soluble and less reactive form of hydrous chromic oxide has very naturally been attributed to the existence of definite allotropic or isomeric modifications. This is very unlikely, particularly since there is no inversion point for a soluble and insoluble modification.   Between these two extremes of solubility, it is possible to prepare an indefinite number of hydrous oxides, each differing slightly from the others in water content, in size of particles, in structure of the mass, and consequently, in reactivity with acids and alkalis.[15]   There is no conclusive evidence that the ultimate product of the aging at room temperature will be the hydrous monohydrate.   This is not improbable, however, since the gel aged rapidly at sufficiently high temperature and pressure yields the monohydrate.

The Glow Phenomenon

Like hydrous ferric oxide, chromic oxide exhibits the glow phenomenon if heated rapidly to temperatures around 500°.   The thermal value is 8–10 calories per gram depending on the conditions of precipitation.[16]   If the rate of heating is very slow or if the gel is kept for some time below the glow temperature, the decrease in specific surface

[14] Compt. rend., **168**, 59, 89 (1919).

[15] Fricke and Windhausen: Z. anorg. Chem., **132**, 273 (1924); Klanfer and Pavelka: Kolloid-Z., **57**, 324 (1931); Lottermoser and Lottermoser: Kolloid-Beihefte, **38**, 1 (1933).

[16] Wöhler: Kolloid-Z., **11**, 241 (1912); **38**, 97; Wöhler and Rabinovich: 111 (1926).

is gradual and is not accompanied by incandescence. The glowing is thus the visible manifestation of the coalescence of primary particles into larger masses with a lower specific surface. Similarly, at ordinary temperatures the gradual change in solubility, in reactivity, and in molar heat of solution in hydrochloric acid is due to coalescence of the small primary particles into larger primary particles with the concomitant diminution in specific surface. The change is a truly irreversible process, differing from ordinary coagulation in which the primary particles merely form secondary aggregates with very little change in specific surface.

Color

Hydrous chromic oxide can be obtained in various shades from a clear gray-blue to a dark green. Certain of these colors, such as chrome green and Guignet's green, constitute the most permanent green pigments. The color of the oxide freshly precipitated in the cold is variously described by different people as bluish, violet-blue, clear blue, clear gray-blue, and gray-violet. The shade differs somewhat, depending on whether it is precipitated from a green or violet chromic salt. On drying the precipitate, the color changes to a distinct green, and the amorphous oxide is described as vivid green. Mention has been made of the transformation of the ordinary precipitated oxide into a product resembling Guignet's green in appearance by heating in an autoclave at 180–250°. Although the color is the same, Guignet's green is a hydrous oxide which gives no x-ray pattern, whereas the green preparation formed in the autoclave is a monohydrate which gives a definite x-ray pattern.

The rate of precipitation has a marked effect on the color of the hydrous oxide. Thus, Casthelaz and Leune[17] claim to have prepared an oxide with a richer and purer color than Guignet's green, simply by slow precipitation at ordinary temperatures of a green solution of a chromic salt with aluminum hydroxide, zinc carbonate, zinc sulfide, or zinc. This observation was confirmed[18] by adding mossy zinc to a solution of green chromic chloride and allowing to stand at 25° for several days. The clear dark green oxide which formed was much more granular than the gray-blue gelatinous oxide obtained by rapid precipitation; moreover, it was quite insoluble in N H_2SO_4.

Berzelius[19] believed the oxides precipitated from violet and green

[17] Bull. soc. chim. (2) 10, 170 (1868).
[18] Weiser: J. Phys. Chem., 26, 410 (1922).
[19] "Lehrbuch," 5th ed., 2, 315 (1848).

solutions to be isomers, since they redissolved in acids giving solutions with the original colors. This, however, seems to depend somewhat on the method of procedure. Thus Recoura[20] added alkali to a green solution until a precipitate formed which was dissolved at once in hydrochloric acid giving a violet solution; and the hydrous oxide precipitated from what Recoura claimed to be Cr_2OCl_4 gave a green solution. However, since the green and violet anhydrous chromic chlorides have different crystal structure, it is perfectly possible to have two isomeric forms of chromic oxide. Unfortunately, this cannot be determined by x-ray diffraction methods since the precipitates from both the green and violet salts give no pattern. To account for the red color of the ruby, Stillwell[21] assumed a red modification of chromic oxide having the same crystal structure as the green but with an axial ratio nearer to that of α-Al_2O_3 than is the axial ratio of the green modification. There is no independent evidence of the accuracy of this assumption. Blanc[22] believes that the difference between the blue and the green oxide is that the former is amorphous and the latter crystalline, but as already indicated, we have no evidence that Guignet's green is crystalline.

Hantzsch and Torke[4] consider the blue-green hydrous oxide from the violet chloride, $[Cr(OH_2)_6]Cl_3$, to have the composition $Cr(OH_2)_3(OH)_3$ or $Cr(OH)_3 \cdot 3H_2O$, and the darker blue-green gel from the green chloride, $[Cr(OH_2)_4Cl_2]Cl \cdot 2H_2O$, to have the composition $Cr(OH_2)(OH)_3 \cdot 2H_2O$ or $[Cr(OH)_3 \cdot H_2O] \cdot 2H_2O$. Since the evidence for the existence of such hydrates is based on dehydration curves obtained by faulty technique (p. 127), the only reason for assigning the above formulas to the hydrous oxides is that they correspond with the Werner formulas of the chlorides from which they were derived. Until definite hydrates of chromic oxide have been shown to exist, nothing is gained by writing formulas for alleged hydrates.

The wide difference in color between the gray-blue precipitated oxide and Guignet's green caused Wöhler and Becker[10] to regard the two substances as hydrate isomers bearing a relation to each other similar to the relationship between blue and green chromic chloride. In support of this view, they showed that two preparations with the same water content had a different vapor pressure, and that the ordinary oxide could be converted into a product resembling Guignet's

[20] Ann. chim. phys. (6) **10**, 1 (1887); *cf.* Olie: Z. anorg. Chem., **52**, 48 (1907).

[21] J. Phys. Chem., **30**, 1441 (1926); *cf.* O'Leary, Royer, and Papish: Science, **80**, 412 (1934).

[22] Ann. chim. (10), **6**, 182 (1926).

green in color by heating in an autoclave. These evidences are altogether inconclusive. In the first place, the vapor pressure of a hydrous oxide is determined not only by the amount of water it contains but also by its structure;[23] and since the conditions of forming Guignet's green and the ordinary oxide are so different, it is not surprising to find variation in the size of the particles and the structure of the masses of each, as is evidenced not only by difference in vapor pressure but also by difference in color. In the second place, Wöhler and Becker were comparing a hydrous oxide with a green crystalline monohydrate and not with the true Guignet's green which is an amorphous hydrous oxide. Finally, there is no inversion temperature of gray-blue oxide to green oxide; this transformation is continuous and is accompanied by a change from a gelatinous to a granular character and by a decrease in the ease of solution and peptization by acids and alkalis.[24]

Adsorption

Observations on adsorption by chromic oxide gel have been concerned primarily with its use in the dyeing and tanning processes which will be considered in later chapters. Adsorption during coagulation of sol will be taken up on page 142.

On account of the extremely fine subdivision of the particles, hydrous chromic oxide is in general a much stronger adsorbent than the corresponding oxides of iron and alumina.[25] The taking up of both acids and bases by the gel can be represented by the adsorption isotherm.[26] Because of the adsorption of most substances by the hydrous oxide, the quantitative estimation of chromium as the oxide is seldom practicable. When the oxide is thrown down in the presence of calcium or magnesium the amounts carried down increase with their concentration and tend toward limits corresponding with the chromites $Cr_2O_3 \cdot 3CaO$ and $Cr_2O_3 \cdot 3MgO$.[27] In this case, the adsorbed impurities may be removed by washing with boiling 5% NH_4NO_3. Adsorbed mono- and di-basic acids may be removed by washing with 5% NH_4HCO_3.[28]

The adsorption of ammonia by a fairly dry chromic oxide gel[29]

[23] Van Bemmelen: "Die Absorption," 239 et seq. (1910).
[24] Weiser: J. Phys. Chem., 26, 409 (1922).
[25] Sen: J. Phys. Chem., 31, 922, 1840 (1927); Z. anorg. Chem., 182, 118, 129 (1929).
[26] Wintgen and Weisbecker: Z. physik. Chem., A135, 182 (1928).
[27] Toporescu: Compt. rend., 172, 600 (1921).
[28] Charriou: J. chim. phys., 23, 673 (1926).
[29] Nikitin: Z. anorg. Chem., 155, 358 (1926).

is less than that for the corresponding ferric oxide and alumina gels, but this is probably due to greater sintering of the former than of the latter during dehydration. A very highly active gel is formed by heating chromium nitrate at 250° in a stream of hydrogen. The adsorption isotherms for sulfur dioxide are completely reversible, no reaction occurring at any temperature, and the amount of adsorption is much greater than for platinum or ferric oxide adsorbents.[30]

CHROMIC OXIDE SOL

FORMATION

Positive Sols by Hydrolysis Methods

Hydrolysis of Chromic Acetate and Ethylate. If a solution of a ferric or aluminum salt is boiled with sodium acetate, the metallic acetate which is formed hydrolyzes, precipitating the respective hydrous oxides. As we have seen, ferric oxide and alumina sols are formed by hydrolysis of the acetates, but chromic oxide behaves differently.[31]   Reinitzer[32] boiled a solution of chromic chloride and sulfate with sodium acetate for a short time, obtaining violet solutions but no precipitate. These solutions were not precipitated in the cold with sodium or potassium hydroxide, ammonia, ammonium hydrosulfide, ammonium carbonate, sodium phosphate, barium hydroxide, or barium carbonate, but were thrown down in the hot by all the above reagents except sodium phosphate. A similar solution which gave no test for chromic ion was obtained by allowing the solution of chromic salt and sodium acetate to stand in the cold for a sufficient length of time. A slow action in the cold in the presence of alkalis is evidenced by a change in color of the solution and the formation of a jelly on standing quietly.

Although some colloidal hydrous chromic oxide may be formed by boiling a chromic salt solution with sodium acetate, it is altogether probable that this process results chiefly in the formation of one or more of the complex chromic acetates, a number of which have been isolated in a definite crystalline form by Werner,[33] and by Weinland and his pupils.[34] Solutions of these salts do not give the usual

[30] Neumann and Goebel: Z. Elektrochem., **39**, 672 (1933).

[31] Schiff: Ann., **124**, 168 (1862).

[32] Monatsh., **3**, 257 (1882).

[33] Ber., **41**, 3447 (1908).

[34] Ber., **41**, 3236 (1908); **42**, 2997, 3881 (1909); Z. anorg. Chem., **67**, 167; **69**, 158, 217 (1910); **75**, 293 (1912); **82**, 426 (1913).

reactions for chromic ion since the chromium is a constituent of a complex ion. It is interesting that, in the presence of excess violet chromic acetate, iron and aluminum acetates cannot be detected either by heating to the boiling point or by adding caustic alkalis or ammonia. As will be pointed out later, hydrous chromic oxide peptized by hydroxyl ion adsorbs and so carries into colloidal solution a number of hydrous oxides not peptized by alkalis. This suggests that hydrous ferric oxide formed by hydrolysis of ferric acetate is kept from precipitating, owing to adsorption by colloidal hydrous chromic oxide. This suggestion does not seem to be in accord with the facts. In the first place, hydrous chromic oxide does not appear to be the primary product of the hydrolysis of chromic acetate; and in the second place, Reinitzer[35] showed that green chromic acetate formed by boiling and so hydrolyzing the violet salt does not prevent the precipitation of hydrous ferric oxide. This behavior of mixtures of ferric and violet chromic acetates is most likely due to the formation of one or more iron-chromic acetate complexes such as have been prepared by Weinland and Guzzmann.[36]

Reinitzer[37] and Woudstra[38] claim to have made hydrous chromic oxide sol by dialysis of chromic acetate, but the extraordinary stability of the preparations in the presence of salts points to their being the unchanged acetate chiefly. This view is supported by a later attempt of Neidle and Barab[39] to dialyze a chromic acetate solution into which superheated steam was passed. Although such a procedure would favor the growth of any particles of colloid, all the chromium passes through the membrane.

A very stable electrolyte-poor sol containing 0.015% Cr_2O_3 results on adding a dilute alcoholic solution of chromic ethylate[40] to water. The particles which carry a weak positive charge vary in size between 3 and 30 mμ.

Hydrolysis of Chromic Chloride and Nitrate. It is not possible to prepare a chromic oxide sol by dialysis of pure chromic chloride in the cold,[41] but the commercial salt yields a dilute sol. The difference in behavior is probably due to acceleration of hydrolysis of the com-

[35] J. Chem. Soc., **42**, 825 (1882).
[36] Ber., **42**, 3881 (1909).
[37] Monatsh., **3**, 249 (1882).
[38] Kolloid-Z., **5**, 33 (1909).
[39] J. Am. Chem. Soc., **38**, 1961 (1916).
[40] Thiessen and Kandelaky: Z. anorg. Chem., **181**, 285; **182**, 425 (1929).
[41] Neidle and Barab: J. Am. Chem. Soc., **39**, 71 (1917).

mercial chloride by the presence of a little colloid as impurity.[42] Since the temperature coefficient of hydrolysis of chromic chloride is considerable,[43] very much higher yields are obtained by dialysis at 75 to 80°. The sols are clear, deep green, and perfectly mobile when first prepared; but they gel on standing if the dialysis is carried too far.

Since nitrate ion usually has a smaller precipitating action on positive sols than chloride ion, Biltz[44] attempted to prepare sols of a number of oxides by dialysis of nitrate solutions. This met with little success with chromium nitrate, on account of the relatively small hydrolysis constant of the salt.[45]

Positive Sols by Peptization Methods

Chromic oxide sol may be prepared by Graham's[46] method: peptization of the freshly precipitated and washed oxide in chromic chloride or chromic nitrate followed by dialysis to remove excess electrolyte. Hydrochloric or nitric acid may be substituted for the respective salts. A fairly pure sol may be obtained without dialysis by adding an excess of gel which will adsorb most of the excess peptizing electrolyte.[47] A Graham sol as strong as 125 g Cr_2O_3 per l has been prepared by Mittra and Dhar.[48] The viscosity of the sol is quite high, and it increases with increasing purification by dialysis until a stiff jelly results. The sol is reversible since the air-dried solid from the sol swells in contact with water and is repeptized.

Probably the simplest method of preparing a chromic oxide sol consists in adding ammonia slowly to pure chromic chloride solution free from sulfate until the precipitate which first forms just fails to dissolve, and dialyzing in the hot to the desired purity with a continuous dialyzer.[49]

Neidle and Barab[49] investigated the dialysis of a Graham sol containing a large excess of the peptizing electrolyte. The sol was placed in a parchment membrane surrounded by water. In one series of experiments the water was changed at intervals; and in a second series, a continuous flow of water through the dialyzer was maintained. Colloidal particles diffused through the membrane in

[42] Goodwin and Grover: Phys. Rev. (2) 11, 193 (1900).
[43] Bjerrum: Z. physik. Chem., 59, 343 (1907).
[44] Ber., 35, 4431 (1902).
[45] Woudstra: Kolloid-Z., 5, 33 (1909).
[46] Phil. Trans., 151, 183 (1861).
[47] Lisiecki: Roczniki Chem., 10, 736 (1930).
[48] J. Indian Chem. Soc., 9, 315 (1932).
[49] Neidle and Barab: J. Am. Chem. Soc., 38, 1962 (1916); 39, 71 (1917).

both cases. In the intermittent dialysis, the sol continued to diffuse until but little remained within the membrane, whereas in the continuous process, the passage of the sol ceased after a time, and 75% remained within the membrane. The growth of the colloidal particles during dialysis was influenced by two factors: agglomeration following removal of peptizing agent, and growth of nuclei by hydrolysis of adsorbed chloride by adsorbed water. In the intermittent process, the removal of peptizing agent was not rapid enough to cause sufficient agglomeration to prevent the passage of the particles through the particular membrane; but in the continuous process, a gradual growth of the particles resulted finally in their retention by the membrane. By continuous dialysis at a high temperature the time required to get a sol containing a minimum amount of peptizing agent may be shortened by weeks.

Paal[50] prepared a sol of hydrous chromic oxide by reduction of a solution of ammonium chromate with colloidal platinum in the presence of the sodium salt of protalbinic acid which acts as a protecting colloid. The preparation contained colloidal hydrous oxide, colloidal platinum, unchanged ammonium chromate, and sodium protalbinate. It may be purified to some extent by dialysis.

The Negative Sol by Peptization Methods

If an excess of alkali hydroxide is added in the cold to a chromic salt solution, the precipitate first formed is peptized completely, giving a clear green sol. In this respect, hydrous chromic oxide differs from hydrous aluminum oxide which dissolves in alkali hydroxides, giving aluminate. The sol formed in this way precipitates spontaneously on standing,[51] particularly if the ratio of oxide to hydroxyl ion is too large. This is due to aging of the hydrous oxide. For the same reason, a precipitated and washed oxide is not readily peptized by alkalis.[52] The sol migrates to the anode under electrical stress,[53] is precipitated by low concentrations of salts having strongly adsorbed cations,[54] and the oxide particles can be removed by an ultrafilter.[55]

[50] Ber., **47**, 2211 (1914).

[51] Fischer and Herz: Z. anorg. Chem., **31**, 352 (1902); Herz: **28**, 344 (1901); **32**, 357 (1902).

[52] Hantzsch: Z. anorg. Chem., **30**, 338 (1902); cf., however, Herz: **28**, 344 (1901).

[53] Kremann: Z. anorg. Chem., **33**, 87 (1903).

[54] Fischer: Z. anorg. Chem., **40**, 39 (1904).

[55] Nagel: J. Phys. Chem., **19**, 331, 569 (1915); Bancroft: Chem. News, **113**, 113 (1916); Trans. Am. Electrochem. Soc., **28**, 357 (1915); Chatterji and Dhar: Chem. News, **121**, 253 (1920).

Further evidence of the colloidal nature of an alkaline solution of chromic oxide is given by its action with other hydrous oxides. Thus Northcote and Church[56] observed that complete solution takes place when chromic oxide is associated with 40% Fe_2O_3, 12.5% MnO, and 20% of either CoO or NiO; and that complete precipitation takes place when chromic oxide is associated with 80% Fe_2O_3, 60% MnO, and 50% of either CoO or NiO. Similar observations were made by Prud'homme,[57] Kreps,[58] and Knoche.[59] The anomalous behavior is readily explained in view of the colloidal nature of alkaline solutions of chromic oxide. The colloidal oxide adsorbs to a limited degree and so carries into colloidal solution the hydrous oxides of iron, manganese, cobalt, nickel, copper, and magnesium, thus preventing their precipitation. The latter oxides likewise adsorb chromic oxide and so tend to take it out of colloidal solution in alkali. Accordingly, if they are present in sufficient amount, they will carry down and so decolorize practically completely the green sol of chromic oxide.[60] As previously noted, the behavior of ferric acetate in the presence of violet chromic acetate cannot be accounted for in this way.

Wood and Black[61] treated precipitated chromic oxide with varying concentrations of alkali. After 2 months some chromate was found in solution, suggesting that chromic oxide dissolves in alkali with the formation of chromite. Since one would expect this action to be more marked if the oxide were in the colloidal state, the author added a large excess of alkali to a chromic chloride solution and allowed the mixture to stand 2 months. Most of the colloid precipitated in this time, leaving a greenish yellow supernatant liquid, the yellow color being due to a small amount of chromate formed by oxidation of chromite in the air. Although these observations show the oxide to possess a slightly acidic character,[62] they do not mean that the solution of hydrous chromic oxide in alkali is all chromite which subsequently decomposes, as Wood and Black imply. On the contrary, it is extremely doubtful whether any chromite at all is formed within a reasonable time in the presence of slightly more than enough alkali to cause complete solution.[63]

[56] J. Chem. Soc., **6**, 54 (1853).
[57] Bull. soc. chim. (2) **17**, 253 (1872).
[58] Thesis, Berlin (1893).
[59] Kolloid-Z., **68**, 37 (1934).
[60] Nagel: J. Phys. Chem., **19**, 331 (1915).
[61] J. Chem. Soc., **109**, 164 (1916).
[62] Cf., also, Müller: Z. physik. Chem., **110**, 363 (1924); Fricke and Windhausen: Z. anorg. Chem., **132**, 273 (1924); Scholder and Pätsch: **220**, 411 (1934).
[63] Weiser: J. Phys. Chem., **26**, 428 (1922); Corey: J. Chem. Ed., **4**, 532 (1927).

The peptization of the gel in the presence of glycerol or cane sugar is accomplished only in the presence of a suitable excess of alkali, which is the real peptizing agent.[64]   Arsenious acid alone does not give a sufficient concentration of anions to peptize the gel as a negative sol.

<div align="center">CONSTITUTION</div>

Chromic oxide sols obtained from chromic chloride are frequently considered to be complex basic salts.   Small amounts of the simple basic salts $Cr(OH)Cl_2$ and $Cr(OH)_2Cl$ were obtained by Bjerrum[65] on adding alkali to chromic chloride,[66] and Recoura[67] claimed to get Cr_2OCl_4 by the oxidation of $CrCl_2$ in the air,[68] but it is unlikely that any quantity of basic salt is present in the well-dialyzed solution of hydrous chromic oxide in chromic chloride.   Neidle and Barab dialyzed such a colloidal solution in the hot until the ratio, equivalents Cr : equivalents Cl, was above 1500.   It seems absurd to regard such a solution as a basic salt; on the other hand, it does not preclude the possible presence of a trace of basic salt in a highly purified sol. For the most part, however, the sol consists of hydrous chromic oxide peptized by preferential adsorption of chromium and hydrogen ions.[69]

If it were possible to dialyze the sol until all the chromic chloride were hydrolyzed and practically all the hydrogen were adsorbed either as hydrogen chloride or as hydrogen ion, the composition of the sol might be represented by the general formula

$$\left[(\boxed{x Cr_2O_3 \cdot y HCl \cdot z H_2O}\ H^+)_n \cdot (n-q)Cl^-\right] + q Cl^-$$
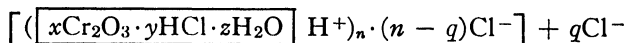
where q represents the excess of adsorbed hydrogen ion over adsorbed chloride ion, that is, the charge on the colloidal particles.   Actually, the solution as well as the sol particles will contain hydrogen ions and may contain chromium ions, and the particles may contain adsorbed chromium.   If hydrochloric acid is placed on one side and a well-dialyzed sol on the other side of a membrane permeable to hydrogen

    [64] Mehrotra and Sen: Kolloid-Z., **42**, 35 (1927).

    [65] Z. physik. Chem., **73**, 724 (1910); *cf.*, *also*, Denham: J. Chem. Soc., **93**, 41 (1908).

    [66] *Cf.* Fischer: Z. anorg. Chem., **40**, 39 (1904).

    [67] Ann. chim. phys. (6) **10**, 1 (1887).

    [68] *See also* Moberg: J. prakt. Chem., **29**, 175 (1843); Loewel: J. Pharm., **4**, 424 (1843); Péligot: Compt. rend., **21**, 74 (1845); Ordway: Am. J. Sci. (2) **26**, 202 (1858); Olie: Z. anorg. Chem., **52**, 62 (1907).

    [69] *Cf.*, *however*, Thomas and von Wicklen: J. Am. Chem. Soc., **56**, 794 (1934).

and chloride ions but not to the colloidal particles holding an excess of adsorbed hydrogen ion, a Donnan equilibrium will be set up with the attending concentration, osmotic, and electrical effects (*cf.* Vol. I, p. 315). Bjerrum[70] placed a chromic oxide sol in a collodion bag and surrounded it by solutions of hydrochloric acid of varying concentration. The outside solution was renewed daily until equilibrium was established, and the osmotic pressure and membrane potential were measured in a special apparatus. From these data Bjerrum calculated that the sol which he employed contained 1000 chromium atoms carrying a total of 240 positive charges, 210 of which were neutralized by adsorbed chloride ion. This is probably incorrect, as a part of the chloride was doubtless adsorbed as salt and not as ion.

The composition of sols, prepared by the incomplete precipitation of chromic chloride with ammonia, was estimated by Wintgen and Löwenthal[71] from electrical conductivity and transport measurements on the sol and the ultrafiltrate therefrom. The composition of a certain sol was formulated ($[20.8Cr_2O_3 \cdot 1.07NH_4Cl \cdot xH_2O]CrO_n^+$) $+nCl$; but because of errors inherent in the method of procedure (p. 58), one can have little confidence in the formula.

Richards and Bonnet[72] digested hydrous chromic oxide with chromium sulfate on the steam bath for several hours, obtaining a green solution which appeared to them to be a basic salt, $Cr(OH)SO_4$. A violet solution shaken for several days with hydrous chromic oxide changed to green which has a composition that could be expressed by the formula $Cr_3(OH)_7(SO_4)_4$. Although these observations prove nothing one way or the other, they indicate that chromic sulfate solution peptizes rather than reacts with hydrous chromic oxide. Seymour-Jones[73] reduced a solution of sodium bichromate with sulfur dioxide, obtaining a solution which dialyzed completely through collodion membranes and passed unchanged through a hardened ultrafilter. Such a solution should have a basicity equivalent to $Cr(OH)SO_4$, but according to Bassett[74] it contains a mixture of 95–96% $Cr_2(SO_4)_3$ and 4–5% chromium dithionate. Hence, the existence of a basic salt of the formula $Cr(OH)SO_4$ has not been established. If such a basic salt was present in Seymour-Jones' solution, it was readily dialyzable, a circumstance that would argue against the presence of

[70] Z. physik. Chem., **110**, 656 (1924).
[71] Z. physik. Chem., **109**, 378 (1924).
[72] Z. physik. Chem., **47**, 29 (1904).
[73] Ind. Eng. Chem., **15**, 77 (1923).
[74] J. Chem. Soc., **83**, 692 (1903).

any basic chloride, $Cr(OH)Cl_2$, in the well-dialyzed Graham sol. Werner[75] isolated a crystalline basic sulfate of the formula $[Cr(OH)_2-(H_2O)_4]_2 SO_4$, but this was done in a special way.

The nature of the basic solutions of chromic sulfate is of interest in connection with chrome mordanting and chrome tanning, which will be taken up in detail in Chapters XV and XVII, respectively.

As already indicated, negative sols contain little or no chromite, the hydrous oxide being held in the sol state as a result of preferential adsorption of hydroxyl ions.

STABILITY

The particles are more highly hydrous in a positive chromic oxide sol than in the corresponding ferric oxide or alumina sol. Because of this hydrophilic character, one would expect the former to be relatively more stable than the latter for the same concentration and particle charge. Although this is true, the stability of the sol is due primarily to its charge, and it behaves toward electrolytes as a typical hydrophobic sol. Freezing precipitates the sol irreversibly unless an excess of peptizing electrolyte is present.[76]

Coagulation by Electrolytes

Precipitation Values for the Positive Sol. A well-dialyzed sol prepared by Graham's method is very sensitive to the presence of electrolytes, particularly if they contain multivalent cations. The

TABLE IX

PRECIPITATION VALUE OF SALTS

Potassium salt	Precipitation value, milli-equivalents per liter	Nature of precipitate	Potassium salt	Precipitation value, milli-equivalents per liter	Nature of precipitate
Ferricyanide.	0.485	Firm jelly	Bromate....	19.0	Jelly
Chromate...	0.525	Firm jelly	Chloride.....	30.0	Jelly
Dichromate..	0.535	Firm jelly	Bromide.....	33.0	Jelly
Sulfate......	0.550	Firm jelly	Chlorate....	33.8	Jelly
Oxalate.....	0.590	Firm jelly	Iodide......	37.5	Jelly
Iodate......	0.635	Firm jelly			

[75] Ber., **41**, 3447 (1908).
[76] Lottermoser and Langenscheidt: Kolloid-Z., **58**, 336 (1932).

precipitation value of a number of potassium salts arranged in the order of decreasing precipitating power for a sol containing 3.65 g Cr_2O_3 per 1 are given in Table IX.[77]   It will be noted that iodate behaves like a multivalent ion in having a very high precipitating power.   It is not obvious why this should be, since a dilute solution of iodic acid acts like a monobasic acid.[78]   It is noteworthy that the conditions at the precipitation concentration are favorable to the formation of a jelly.   This point will be considered in a later section. The jellies can be broken up by shaking, yielding gelatinous precipitates.

The stability of the sol as measured by the precipitation values of electrolytes increases with increasing hydrogen ion concentration up to a pH value of about 2.5.[79]

Precipitation Values for Negative Sol.   In Table X are given the precipitation values of several electrolytes for a negative sol

TABLE X

PRECIPITATION VALUES OF SALTS

Salt	Precipitation value, milliequivalents per liter	Nature of precipitate
Barium chloride........	5.15	Gelatinous
Potassium chloride.....	500.0	Gelatinous
Sodium chloride........	210.0	Gelatinous
Lithium chloride.......	51.0	Gelatinous
Sodium sulfate.........	315.0	Gelatinous
Sodium acetate.........	220.0	Gelatinous

prepared by mixing 5 cc of $CrCl_3$ containing 40 g Cr_2O_3 per 1 with 45 cc of 0.2 N KOH.   The precipitation value is that concentration of electrolyte which will just cause complete coagulation in 10 minutes. It will be noted that the precipitating power of cations follows the usual order: barium > lithium > sodium > potassium;   and the stabilizing action of the anions is: sulfate > chloride > acetate.

[77] Weiser: J. Phys. Chem., **26**, 418 (1922).

[78] Miolati and Mascetti: Gazz. chim. ital., **31** I, 93 (1901); Giolitti: Atti accad. Lincei (5) **14** I, 217 (1905).

[79] Weiser and Porter: J. Phys. Chem., **31**, 1383 (1927); cf., *also*, Bedford, Keller, and Gabbard: J. Am. Chem. Soc., **55**, 3953 (1933).

Adsorption During Coagulation

Adsorption of Sulfate. Since the stability of a sol is increased by increasing its hydrogen ion concentration, one would expect the adsorption of precipitating ions to be influenced by the pH value of the sol. This is illustrated by some observations on the adsorption of sulfate during the coagulation of a Graham sol containing 2.5 g Cr_2O_3 per l. Typical data are given in Table XI and shown graphically in Fig. 24. It will be seen that raising the concentration of the

TABLE XI

ADSORPTION OF SULFATE BY HYDROUS CHROMIC OXIDE AT VARYING pH VALUES

Cc of soln. mixed with 50 cc of sol containing 0.125 g of Cr_2O_3 in a total of 200 cc			Adsorption values, milliequivalents per g Cr_2O_3	pH values	
$N/50$ H_2SO_4	$N/50$ K_2SO_4	$N/50$ KOH		Before adsorption	After adsorption
50	0	0	4.66	2.42	2.87
40	10	0	4.60	2.49	2.97
30	20	0	4.52	2.59	3.15
20	30	0	4.28	2.73	3.64
10	40	0	3.48	3.09	5.15
0	50	0	1.90	8.68	8.29
0	50	5	1.28	10.61	8.73
0	50	10	0.48	10.95	8.96
0	50	20	−0.08	11.28	9.39
0	50	30	−0.10	11.41	9.87

hydrogen ion increases the positive charge on the particles, thereby increasing their capacity to adsorb sulfate. The adsorption of the sulfate falls off quite rapidly with increasing concentration of the hydroxyl ion, the carrying down of the sulfate being completely nullified at a pH value of about 9.2. It is obvious, however, that both sulfate and hydroxyl are adsorbed in the alkaline range from a pH of 7.0–9.0. In Loeb's investigations on the proteins[80] it seems probable that he overlooked the specific effect of cations other than hydrogen and of anions other than hydroxyl, since he worked with relatively low concentrations of salts. The pH-adsorption curve is

[80] Loeb: "Proteins and the Theory of Colloidal Behavior," 2nd ed. (1924).
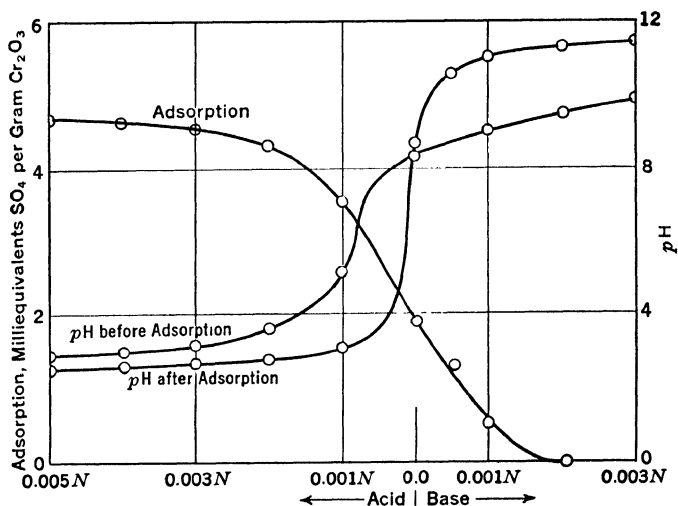
FIG. 24.—Adsorption of sulfate by hydrous chromic oxide at varying pH values.
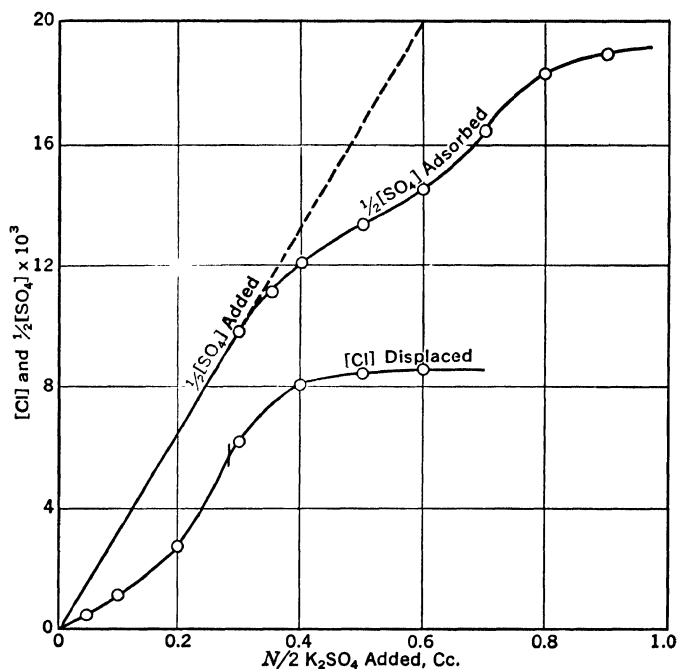
FIG. 25.—Simultaneous displacement of chloride and adsorption of sulfate on titrating chromic oxide sol with K_2SO_4.

smooth throughout, showing no indication of the formation of a compound between the sulfate and the aged hydrous oxide even at pH values as low as 2.0.

Since the mechanism of the coagulation process is essentially the same for chromic oxide sol as for ferric oxide or alumina sol, one would expect a simultaneous displacement of chloride during the adsorption of the precipitating ion.[81]   This is shown by observations represented graphically in Fig. 25.   The form of the curves and the relationship of the displacement to the adsorption curve are similar to those observed with colloidal alumina, and for the same reason (p. 115).

Simultaneous Adsorption of Sulfate and Oxalate.   Miller[82] studied the simultaneous adsorption of oxalate and sulfate by alumina (p. 102) and arrived at the conclusion that the adsorption was a solid solution phenomenon since the concentration of oxalate (or sulfate) in the solution divided by its concentration in the adsorbent was a constant. This conclusion is not justified, since the maximum value for the alleged constant was more than a thousand times the minimum value. Moreover, even if these values had been constant, his data would not have justified his conclusion, since the pH value was allowed to vary through wide limits, and this is the determining factor in the particular range that Miller happened to work in.   It should be noted further, that as the ratio of total sulfate to oxalate fell off, the value for the sulfate constant increased, the increase being very rapid as equal concentrations of sulfate and oxalate were approached.   Had Miller taken ratios of oxalate to sulfate greater than one, the so-called constant for sulfate would have been found to approach infinity very rapidly, for in a neutral solution, the adsorption of sulfate becomes zero in the presence of an appreciable excess of oxalate.   This is illustrated by some comparable data on the simultaneous adsorption of sulfate and oxalate by hydrous chromic oxide, recorded in Table XII.[83]   In these observations the adsorption of 25 cc of the $N/50$ solution corresponds to 1.77 milliequivalents per g Cr_2O_3.

Since the precipitation concentration as well as the adsorption of oxalate and sulfate are so nearly equal, one might be led to conclude that their adsorptions would be nearly equal when both are present in the same solution.   This is not even approximately true if the solution is neutral or basic.   In order to get any measurable quantity

[81] Weiser and Gray: J. Phys. Chem., **36**, 2178 (1932).
[82] U. S. Pub. Health Repts., **39**, 1502 (1924).
[83] Weiser and Porter: J. Phys. Chem., **31**, 1383 (1927).

TABLE XII

Adsorption by Hydrous Chromic Oxide from Mixtures of
Oxalate and Sulfate

Cc of soln. mixed with 50 cc of sol containing 0.283 g Cr_2O_3 in a total of 150 cc		Adsorption in milliequivalents per g of Cr_2O_3			pH after adsorption
$N/50$ $K_2C_2O_4$	$N/50$ K_2SO_4	Oxalate	Sulfate	Total	
50	0	2.13	0.0	2.13	8.30
60	0	2.17	0.0	2.17	8.37
50	25	2.09	−0.03	2.06	
50	50	2.04	0.14	2.18	8.11
25	50	1.45	0.46	1.90	7.68
10	50	0.65	1.30	1.95	7.49
0	50	0.00	1.86	1.86	7.32
25	25	1.63	0.36	1.99	7.97

of sulfate adsorbed at a pH of 8.0, it is necessary to have a very low concentration of oxalate, and to get equivalent adsorptions at this pH value, the final concentration of sulfate must be approximately 128 times that of oxalate. The conclusions to be drawn from these data are: first, under the same conditions, the equivalent adsorption by the hydrous chromic oxide is approximately equal, whether it be all sulfate, all oxalate, or some of each; second, so long as there is an excess of oxalate in the bath, it displaces the sulfate almost completely, whereas a small excess of sulfate has but little effect on the adsorption of oxalate; third, it is necessary to limit the concentration of the oxalate in order to make a study of the simultaneous adsorption of oxalate and sulfate in a neutral or basic solution.

To determine the effect of varying hydrogen ion concentration on the simultaneous adsorption, a total quantity of oxalate plus sulfate corresponding to 16 milliequivalents per gram of oxide was used. In actual quantities of reagents this is represented by sufficient sol to contain 0.125 g of oxide and 50 cc of each of the $N/50$ solutions. The concentrations are sufficiently high so that, at maximum adsorption, the bath will not be exhausted with respect to either sulfate or oxalate ion. The results are shown graphically in Fig. 26. The form of the adsorption curves show: first, that the oxalate is displaced appreciably by the sulfate when the final solution is but faintly acid; and second,

that the adsorptions approach equivalence in the strongly acid solution. This observed behavior is probably due not to a shift in the relative adsorbability of the bivalent oxalate and sulfate ions but to the relatively greater conversion of bivalent oxalate to the less strongly adsorbed bioxalate ion than of bivalent sulfate to bisulfate ion, in the
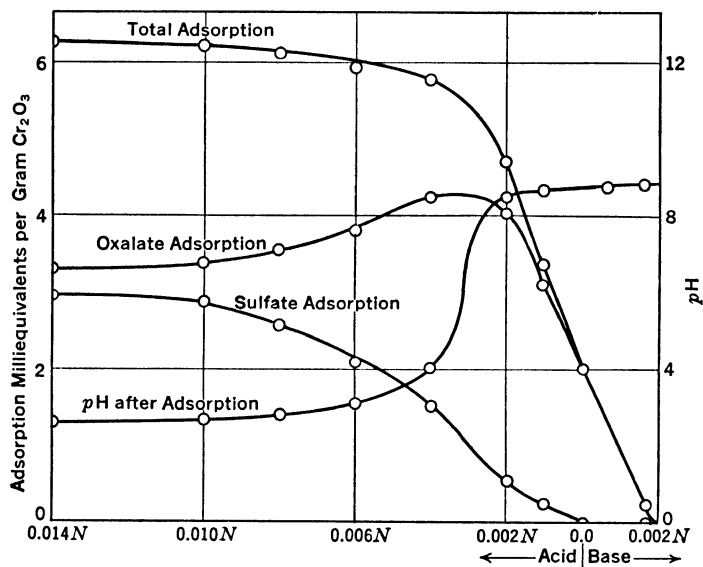
Fig. 26.—Simultaneous adsorption of oxalate and sulfate by hydrous chromic oxide at varying pH values.

acid solution. In Chapter XVI it will be shown that the behavior of oxalate in this respect is similar to that of certain acid dyes.

CHROMIC OXIDE JELLIES

Mention has been made of Reinitzer's observation that a solution of chromic salt, boiled with sodium acetate and rendered alkaline with caustic alkalis or ammonia, sets to a jelly. Bunce and Finch[84] confirmed this observation and showed further that a jelly is formed by adding excess sodium hydroxide or potassium hydroxide to chrome alum and allowing the solution to stand. They were unable to obtain a jelly from chromic sulfate, nitrate, or chloride; but Nagel[85] succeeded in getting a jelly with sulfate by keeping down the concentration of

[84] J. Phys. Chem., 17, 769 (1913).
[85] J. Phys. Chem., 19, 331 (1914).

alkali. From these observations it was logical to conclude that acetate or sulfate ions are necessary for the formation of a chromic oxide jelly.[86] That such is not the case is evident from the series of experiments recorded in Table XIII,[87] using chromic chloride instead of sulfate or acetate. The experiments bear out the general conclusions regarding jelly formation previously considered in detail (p. 14). The rapid addition of a slight excess of alkali to a chromic chloride solution produces a negative colloidal oxide that is instable and precipitates slowly, forming a jelly (Table XIII). If this precipitation is hastened by heating or by addition of a suitable amount of electrolyte, the precipitate forms so rapidly that it is gelatinous and not jelly-like (Table X). Finally, if the hydrous oxide has been peptized by too great a concentration of alkali, the precipitate comes down very slowly and is almost granular in character, as observed by Nagel.

TABLE XIII

CHROMIC OXIDE JELLIES FROM NEGATIVE SOL

Alkali	Solutions mixed, cc			Observations	Nature of precipitate
	Alkali 0.6 N	CrCl$_3$	Total volume		
NaOH	10.0	5.0	25	Peptization incomplete	Gelatinous
NaOH	11.5	5.0	25	Peptization incomplete	Firm green jelly
NaOH	11.75	5.0	25	Peptization almost complete	Firm green jelly
NaOH	12.0	5.0	25	Peptization complete	Firm green jelly
KOH	10.0	5.0	25	Peptization incomplete	Firm green jelly
KOH	10.75	5.0	25	Peptization almost complete	Firm green jelly
KOH	11.0	5.0	25	Peptization complete	Firm green jelly
Ba(OH)$_2$	20.0	5.0	25	No peptization	Gelatinous
Ba(OH)$_2$	24.0	1.0	25	No peptization	Gelatinous
NaOH	13.5	5.0	50	Peptization almost complete	Soft green jelly
NaOH	13.75	5.0	50	Peptization complete	Soft green jelly
KOH	12.0	5.0	50	Peptization almost complete	Soft green jelly
KOH	12.25	5.0	50	Peptization complete	Soft green jelly

The experiments under consideration corroborate the observation of Fischer and Herz that the peptizing power of potassium hydroxide

[86] Bancroft: "Applied Colloid Chemistry," 244 (1921).
[87] Weiser: J. Phys. Chem., **26**, 428 (1922); Prakash: **36**, 2483 (1932); Prakash and Dhar: J. Indian Chem. Soc., **6**, 391 (1929); **7**, 591 (1930).

is slightly greater than that of sodium hydroxide.　On the other hand, they disprove the statement that hydrous chromic oxide is peptized by barium hydroxide and that the peptizing power of alkalis depends on the absolute amount present and not on the concentration.　The hydroxides arranged in order of peptizing power are: KOH > NaOH > Ba(OH)$_2$.　As would be expected, this is the reverse of the order of precipitating power of the cations (Table X).

Knowing the conditions favorable to jelly formation by precipitation of a negative sol, it is a simple matter to precipitate the positive sol as a jelly by adding just enough electrolyte to cause complete coagulation in an hour or two.　If too little electrolyte is used, precipitation is incomplete and the results are unsatisfactory; and if too great an excess is added, the precipitation is so rapid that a gelatinous precipitate is formed.　From the results recorded in Table IX it is quite evident that jellies will form in the presence of any precipitating ion. Moreover, the hydrogen ion concentration within which jellies will form can vary over a wide range; thus, they are obtained from strongly alkaline solution and from a sol stabilized by hydrogen ion.　A typical jelly containing but 0.18% Cr$_2$O$_3$ will stand for days without undergoing noticeable syneresis.　Shaking destroys the jelly structure, which does not re-form as do more concentrated jellies which are thixotropic.[88]

The evaporation of a chromic oxide sol gives a deposit consisting of alternate colored and colorless rings.[89]　This formation of a deposit of lines or filaments separated by clear spaces is characteristic of the hydrophobic colloids.[90]

[88] *Cf.* Schalek and Szegvari: Kolloid-Z., **32**, 318; **33**, 326 (1923).

[89] Bary and Rubio: Compt. rend., **188**, 625 (1929).

[90] Hedges: Chemistry & Industry, **51**, 25 (1932)

CHAPTER V

THE HYDROUS OXIDES AND HYDROXIDES OF COPPER, COBALT, NICKEL, SILVER, AND GOLD

HYDROUS CUPRIC HYDROXIDE

Bivalent copper forms a highly hydrous hydroxide, but the oxide as ordinarily obtained is only slightly hydrous. Monovalent copper, on the other hand, gives a highly hydrous oxide but forms no hydroxide.

CUPRIC HYDROXIDE GEL

FORMATION AND COMPOSITION

The blue gelatinous mass obtained by the addition of dilute alkali to a cupric salt contains as much as 20 mols of water to 1 of cupric oxide when freshly prepared and dried by pressing between porous earthenware. Van Bemmelen[1] showed that exposure of the gel to an artificially dried atmosphere at room temperature causes it to lose water continuously until the vapor pressure is equal to that of the atmosphere. From $\pm 2H_2O$ to $\pm 1H_2O$ the water is held more firmly than above $\pm 2H_2O$, and at a pressure of zero, the composition approaches that of $CuO \cdot H_2O$ or $Cu(OH)_2$. The fresh gel is instable, and if allowed to stand in contact with the mother liquor it loses water and changes in color from blue to green, brown, and, finally, black. In the absence of conclusive evidence to the contrary, it was believed at one time[2] that the blue gel was hydrous CuO rather than $Cu(OH)_2$ and that the variation in color from blue to black was due to differences in particle size. It is now known that such is not the case, for the blue and the black precipitates give entirely different x-ray diffraction patterns. Thus Neville and Oswald[3] obtained the x-ray diffraction pattern, a diagram of which is shown in Fig. 27a, for the blue precipitate thrown down (1) at 0° and dried at room temperature, (2) at

[1] Z. anorg. Chem., **5**, 466 (1894).
[2] Weiser: J. Phys. Chem., **27**, 501 (1923).
[3] J. Phys. Chem., **35**, 60 (1931); cf. Binder: Compt. rend., **198**, 653 (1934).

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room temperature in the presence of gelatin to stabilize it, and dried at 55°, and (3) the same as (2) but not dried.   On the other hand, the pattern shown diagrammatically in Fig. 27b was obtained (1) from the moist black gel which forms spontaneously from the blue gel, (2) from the black product formed by heating the dry blue powder to 105°, and (3) the same as (2) dried over a Bunsen burner.   These observations confirm the work of Posnjak,[4] who showed further that the blue gel has the same crystal structure as the microscopically crystalline preparations which are known to have the composition $CuO \cdot H_2O$.   Finally, Neville and Oswald showed that a green powder obtained by drying the blue gel at 95°C was not another hydrate but gave an x-ray diffraction pattern containing lines corresponding to both the blue and the black compounds.   It therefore appears that
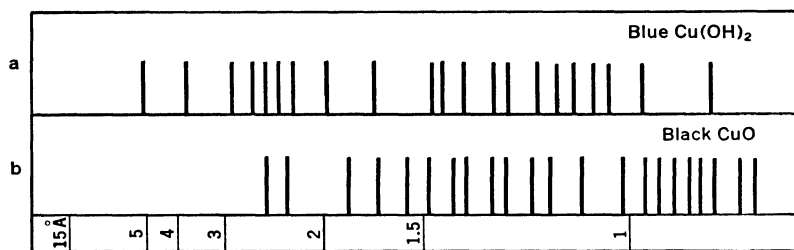
FIG. 27.—Diagrams of the x-ray diffraction patterns of (a) $Cu(OH)_2$ and (b) CuO.

the colored products intermediate between blue and black are mixtures of $Cu(OH)_2$ and CuO in varying amounts.   The brown oxide formed during the dehydration process is not $4CuO \cdot H_2O$ but CuO with adsorbed water or a mixture of CuO and $Cu(OH)_2$.[5]

The microscopically crystalline $Cu(OH)_2$ is prepared (1) by the action of dilute alkali on a basic cupric nitrate,[6] (2) by the action of concentrated alkali on crystalline basic cupric sulfate,[7] and (3) by the hydrolysis of blue-violet copper ammonium nitrate.[8]

[4] Unpublished results reported at the 78th Meeting of the American Chemical Society in Minneapolis, September (1929).

[5] Levi: Giorn. chim. ind. applicata, 12, 97 (1930); Champetier and Thuau: Compt. rend., 194, 93 (1932).

[6] Becquerel: Compt. rend., 34, 573 (1852); cf. van Bemmelen: Z. anorg. Chem., 5, 468 (1894).

[7] Böttger: Jahresber., 198 (1858); Habermann: Z. anorg. Chem., 50, 318 (1906).

[8] Péligot: Compt. rend., 53, 209 (1861); cf. Bonsdorff: Z. anorg. Chem., 41, 132 (1904).

PROPERTIES

Stability of the Blue Hydroxide

The instability of blue gelatinous cupric hydroxide is one of its most characteristic properties. If the gel is thrown down in the presence of a slight excess of alkali, it changes in color through green and brown to black, the process going on slowly at room temperature and with increasing velocity as the temperature is raised. On the other hand, if the gel is thrown down in the presence of a slight excess of copper ion, it does not turn black even at the boiling temperature.[9] Mehrotra and Dhar[10] found that all the copper is precipitated from a solution of cupric sulfate by less than the equivalent quantity of sodium hydroxide, and that either the cupric and sulfate ions are adsorbed in equivalent amounts or some basic salt of the composition $3Cu(OH)_2 \cdot CuSO_4$, or $4CuO \cdot SO_3 \cdot 4H_2O$[10] is formed. It is apparent, therefore, that a copper hydroxide free from basic salt or adsorbed copper salt will be formed only in the presence of a slight excess of alkali. The precipitate will then contain adsorbed alkali which for some unknown reason appears to accelerate the darkening. Hence, to obtain a clear blue product, precipitation should be carried out at 0° and the mother liquor removed by washing with iced water as rapidly as possible.[11]

Unlike the gel, the microscopically crystalline compound is relatively stable in boiling water, maintaining its blue color when heated for hours at 100°. However, it darkens gradually on long standing even at room temperature. Thus 10-year-old samples made by the methods of Böttger and Péligot, above referred to, were reported by Fowles[12] to have a bluish slate tint; and a 12-year-old sample was quite black.

Although alkalis and certain alkali salts tend to decrease the stability of the blue gelatinous oxide, Tommasi[13] found a retardation of the blackening in the presence of a number of salts, notably manganous sulfate. Bancroft[14] attributed the stability to adsorption of the hydrous oxide of manganese which acts as a protecting colloid.

[9] Chatterji and Dhar: Chem. News, **121**; 253 (1920).

[10] J. Phys. Chem., **33**, 216 (1929); Binder: Compt. rend., **198**, 653 (1934).

[11] Villers: Compt. rend., **120**, 322 (1895).

[12] Chem. News, **128**, 2 (1924).

[13] Bull. soc. chim. (2) **37**, 197 (1882); Compt. rend., **99**, 38 (1884).

[14] J. Phys. Chem., **18**, 118 (1914).

Although this conclusion was reaffirmed by Blucher and Farnau[15] as a result of observations with salts of a number of heavy metals other than manganese, it seems questionable,[2] since (1) relatively high concentrations of colloidal hydrous oxides are not effective, and (2) copper sulfate is as effective as manganous sulfate or chromic sulfate. The first experiment is not especially impressive, since there is no necessary reason why the adsorption of a colloidal oxide by the separately precipitated copper oxide gel should give the same result as adsorption of the oxide from a salt solution; but the second observation is fairly conclusive, since it is inconceivable that blue hydrous cupric oxide should stabilize itself.[2] Inasmuch as the only salts effective in low concentration are those which give an acid reaction by hydrolysis, there still remains the possibility that the stabilizing agent is a basic salt.[16] Fowles believes that the stabilizing effect of such salts as the sulfates of copper, manganese, and chromium results from the removal of adsorbed alkali (an accelerator) and the formation of basic cupric salts which are very stable. Since adsorption of a stable basic salt would tend to stabilize the blue gel, it is unnecessary to assume that all the gel is converted to basic salt. Gelatin is strongly adsorbed by the blue gel and is quite effective in stabilizing it.

Altogether apart from the presence of adsorbed protecting agents, the stability of copper hydroxide is greater the older and denser the mass and the larger the crystals. As we have seen, a gel aged at $0°$ is fairly stable, and a precipitate composed of relatively large crystals is quite stable. Observations disclose that the decomposition starts spontaneously at some nucleus and spreads in all directions from this point. The minute, insoluble particles of copper oxide in commercial copper nitrate solutions act as centers to initiate the transformation. The reaction doubtless occurs at the interface between the two solid phases CuO and $Cu(OH)_2$, just as the reduction of CuO occurs at the interface Cu-CuO.[17] It would be expected that the spreading of the dehydration process would extend more readily through a moist gel composed of extremely minute crystals than through a granular mass composed of larger crystals.

Kohlschütter and Tüscher[18] believe that the dehydration is not a simple molecular splitting off of water: $Cu(OH)_2 \rightarrow CuO + H_2O$, but

[15] J. Phys. Chem., **18**, 629 (1914).

[16] Krüger: J. prakt. Chem. (2) **108**, 278 (1924).

[17] Pease and Taylor: J. Am. Chem. Soc., **43**, 2179 (1921); Jones and Taylor: J. Phys. Chem., **27**, 623 (1923).

[18] Z. anorg. Chem., **111**, 193 (1920).

depends on intramolecular neutralization of the H^+ and OH^- ions resulting from amphoteric dissociation of the hydroxide as follows:

$$Cu^{++} + 2OH^- \rightleftarrows Cu(OH)_2 \rightleftarrows CuO_2^{--} + 2H^+$$
$$H^+ + OH^- = H_2O$$
$$Cu^{++} + CuO_2^{--} \rightarrow 2CuO$$
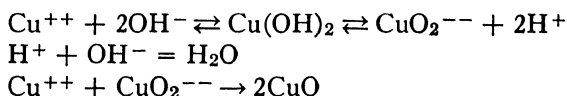
To account for the facts, it is assumed that this process takes place between molecular complexes large enough to be of colloidal dimensions and that a definite degree of dispersity is necessary for the change. Too low or too high dispersity represses the reaction, and between these extremes the stability falls off with increasing dispersion.   The same primary particles may give a loose aggregate which is favorable to dehydration or a dense aggregate which is more stable.   From this point of view, stabilization by an adsorbed basic salt or gelatin or by low temperature may be looked upon as a process of inhibiting the agglomeration of the primary particles as they are transformed into a compact mass by drying.   This would be equally true whether one assumes that the dehydration is the result of molecular dehydration or of "internal neutralization as a result of amphoteric dissociation."

Like bases, certain alkali salts increase rather than retard the spontaneous dehydration of hydrous cupric hydroxide.   Since the effect is not appreciable except with relatively high concentrations of the salts, it probably results from their dehydrating action.[19]   An alternative hypothesis is suggested by the behavior of hydrous cupric hydroxide toward alkali salts.   Tommasi[20] found that solutions of sodium chloride and sodium sulfate show an alkaline reaction after shaking with the hydroxide, probably owing to hydrolysis of the salts as a result of stronger adsorption of acid than of base.   The slight decrease in stability in the presence of alkali salts may be due to the slight alkalinity of the solution in which the particles are suspended.

Hydrogen peroxide has been found by Quartaroli[21] to accelerate the darkening of hydrous cupric hydroxide suspended in a definite amount of alkali at 50°.   This action is greatly accelerated by 1 part of peroxide in 3 million of water and is still perceptible with 1 part of peroxide in 200 million of water.   In view of the presence of minute traces of hydrogen peroxide in ordinary distilled water, this compound is believed to bring about the spontaneous decomposition of the

[19] Poma and Patroni: Z. physik. Chem., **87**, 196 (1914).

[20] Bull. soc. chim. (2) **37**, 197 (1882); Iyer: J. Indian Chem. Soc., **8**, 613 (1931).

[21] Gazz. chim. ital., **54**, 713 (1924); **55**, 264 (1925); **64**, 243 (1934).

hydrous oxide or, at least, to accelerate the process. Such sensitive action of extremely minute amounts of substance has been found only in the action of copper in provoking the oxidation of sulfites and in the quantity of substance required to break up metastable states. Various electrolytes, especially magnesium salts, retard the blackening when present in amounts hundreds of times less than that of the hydrous oxide, but the action of such electrolytes exhibits striking irregularities. Quartaroli concludes that the blackening of the oxide suspended in alkali solution is not a simple dehydration process but is a phenomenon connected with oxidations and reductions with the formation of saline hydrates containing copper atoms with various grades of oxidation. These observations should be confirmed and extended. Quartaroli's belief that Cu_4O is formed as an intermediate product in the action of copper oxide and hydrogen peroxide is certainly wrong (p. 150).

Color

As we have seen, the results of x-ray analysis show that the blue precipitated compound is copper hydroxide, the black compound formed by dehydration of the blue is cupric oxide, and the products giving intermediate shades of green and brown are mixtures of the blue hydroxide and the black oxide. It is possible that cupric oxide possesses a blue color if sufficiently finely divided. Thus Schenck observed that mixtures of cupric oxide and alumina containing 5% cupric oxide remain blue after ignition, possibly because the cupric oxide is prevented from agglomerating. In one instance[22] the excess alumina was dissolved out with alkali giving a blue powder in which the ratio of CuO to Al_2O_3 was approximately 4 : 1. An x-ray analysis should be made of this product to determine definitely whether the blue color is due to sufficiently finely divided copper oxide or to a copper aluminate.

SOLS OF CUPRIC OXIDE AND HYDROXIDE

Because of the tendency of cupric hydroxide to decompose, giving cupric oxide, sols of the former are instable except in the presence of protecting agents, and even then, the dispersed phase is likely to be a mixture of the hydroxide and oxide as evidenced by the variations in color.

[22] Schenck: J. Phys. Chem., **23**, 283 (1919).

Positive Sols

Protected Sols. Graham[23] prepared a fairly stable sol by adding alkali to a solution of cupric chloride containing cane sugar. It was deep blue at first but changed to green on dialyzing; the precipitate obtained on boiling the sol or on adding salts or acids was bluish green in color. A more stable sol can be prepared using Paal's[24] sodium salts of lysalbinic or protalbinic acids as protector. Other stabilizing agents that have proved effective are agar,[25] casein,[26] milk and grape sugar,[27] starch,[28] and soap. Thorium and uranyl nitrate[29] peptize the gelatinous hydroxide owing to strong adsorption of the salt cations. Biltz[30] attempted to prepare the colloidal oxide by dialysis of a solution of cupric nitrate, but the salt passed unchanged through the dialyzer owing to its low hydrolysis constant. Ley[31] hydrolyzed the copper salt of succinimide, obtaining a very satisfactory sol that changed in color, slowly at room temperature but rapidly at 70°, from blue-green to yellow-brown and finally dark brown. Succinimide is a protector, since its removal by dialysis causes agglomeration of the sol. The kinetics of the hydrolysis process have been studied by Preis and Peskov.[32]

Unprotected Sols. An unprotected sol of cupric oxide is obtained by oxidizing a copper sol[33] and by what Kohlschütter called "discharge electrolysis."[34] In the latter process, a passivifying layer of oxide was deposited on the anode and subsequently dispersed in the liquid by a rapidly oscillating discharge. The sol was perfectly clear in transmitted light; it was bluish green in color at the outset but changed to brown on standing. By means of the ultramicroscope, Kohlschütter[35] observed the formation of blue hydrous cupric oxide sol when a current of relatively high density was passed between

[23] Phil. Trans., **151**, 183 (1861); Compt. rend., **59**, 174 (1864).

[24] Paal and Leuze: Ber., **39**, 1550 (1906); Paal and Steyer: Kolloid-Z., **30**, 1 (1922).

[25] Ludwig: Arch. pharm., **82**, 157 (1855).

[26] Ritthausen: J. prakt. Chem. (2) **5**, 215 (1872); Ritthausen and Pott: **7**, 361 (1873).

[27] Salkowski: Pflügers Arch., **6**, 221 (1872); Sen and Dhar: Kolloid-Z., **33**, 193 (1923).

[28] Breindl and Söllner: Kolloid-Z., **59**, 331 (1932).

[29] Szilard: J. chim. phys., **5**, 636 (1907).

[30] Ber., **35**, 4431 (1902).

[31] Ber., **38**, 2199 (1905); Ley and Werner: **39**, 2178 (1906).

[32] J. Phys. Chem. (U.S.S.R.) **3**, 43 (1932); Kolloid-Z., **61**, 328 (1932).

[33] Lottermoser: "Anorganische Kolloide," Stuttgart (1901).

[34] Kohlschütter: Z. Elektrochem., **25**, 309 (1919).

[35] Z. Elektrochem., **30**, 164 (1924).

copper electrodes dipped in dilute cupric sulfate solution or in water.

The sol formed by passing a spark between copper wires under water, according to Bredig's method, is chiefly copper oxide although it may contain some copper.[36] Stirring accelerates the velocity of coagulation of this sol by electrolytes, particularly when ions of high coagulating power are employed and when the concentration of electrolyte is in the region of the precipitation value. Prolonged stirring alone without the addition of precipitating electrolyte causes coagulation, provided air is stirred into the sol, thereby increasing the extent of air-liquid interface. The particles are so strongly adsorbed at this interface that agglomeration finally results.[37] Raising the temperature decreases the stability of the sol to the coagulation point (Vol. I, p. 140).

The sol formed by Bredig's method is positively charged, the precipitating power of electrolytes being determined largely by the valence of the anion in the usual order: $K_4Fe(CN)_6 > K_2SO_4 > KCl$. Paine[38] found the decrease in mobility of the colloidal particles on adding electrolytes to be directly proportional to the square root of their concentration. The addition of the sodium salts of gallic, salicylic, and tannic acids stabilizes the sol.[39] With small additions of sodium gallate up to 0.006 millimol per liter the charge remains positive, but at higher concentrations it is reversed, probably owing to strong adsorption of gallate or hydroxyl ion. Rochelle salt likewise reverses the charge on the sol and stabilizes it.[40] Breindl and Söllner showed that a small amount of starch changes but slightly the velocity of coagulation of the sol by electrolytes. Larger amounts decrease the velocity greatly up to a critical value above which further additions have little effect. Hooker[41] prepared a very satisfactory blue sol by thorough washing of the gelatinous oxide formed by adding alkali to copper sulfate solution until the supernatant liquid was just colorless. The washing may be carried out by sedimentation, but a more stable sol results by repeated washing with the supercentrifuge.[42]

[36] Burton: Phil. Mag. (6) 11, 436 (1906).

[37] Freundlich and Basu: Z. physik. Chem., 115, 203 (1925); Freundlich and Kroch: 124, 155 (1926); Naturwissenschaften, 14, 1206 (1926); Freundlich and Loebmann: Z. physik. Chem., A139, 368 (1928); Freundlich and Recklinghausen: A157, 325 (1931).

[38] Trans. Faraday Soc., 24, 412 (1928).

[39] Basu and Narasinha-Murty: Kolloid-Z., 56, 51 (1931).

[40] Basu and Lakshmanan: J. Indian Chem. Soc., 4, 29 (1927).

[41] Ind. Eng. Chem., 15, 1177 (1923).

[42] Cf. Bradfield: J. Am. Chem. Soc., 44, 965 (1922).

The colloid has high fungicidal action against apple scab and apple black in concentrations of 1 part of oxide to 5000 of water; at this concentration it causes only very slight burning. This sol possesses excellent sticking properties due to its positive charge and can be used in conjunction with lead arsenate and nicotine sulfate, if desired. Since the sol can be prepared at relatively low cost, it is suggested as a substitute for Bordeaux mixture and lime-sulfur.

Negative Sols

If copper acetate solution is treated with ammonia in less than equivalent amounts and in the presence of sulfate, a negative copper hydroxide sol is obtained which is instable, coagulating after a time to give a gelatinous precipitate or jelly, depending on conditions.[43] The solution of copper hydroxide in excess ammonia is said to be partly colloidal.[44]

Cupric hydroxide gel dissolves but slightly in dilute alkali but is appreciably soluble in concentrated alkali, forming deep-blue solutions.[45] As might be expected, the instable blue gelatinous oxide is more soluble than the black compound, and the latter separates gradually from a solution of the former, provided the alkali (NaOH) concentration does not exceed 17 N.[46] Both copper in the presence of air and anhydrous CuO dissolve in strong alkali, forming blue solutions which are stable on boiling and do not precipitate out on standing.[47] The bulk of the evidence supports the view that the blue coloration is due to CuO_2^{--}[48] ion and not to colloidal cupric oxide. Fischer[49] added alkali to copper salts short of precipitation and obtained blue solutions which were supposed to be colloidal because hydrous copper hydroxide settles out on standing or can be filtered out. The discoloration of the solution by filtering was believed by Creighton to result from interaction between the cellulose of the filter and the blue component, since the filtrate was blue after several portions were passed through the same filter. This observation is not quite conclusive, since the filter may have become more porous owing to peptization of the filter paper by the alkali. However, Müller prepared

[43] Weiser: J. Phys. Chem., **27**, 685 (1923); cf. Foerster: Ber., **25**, 3416 (1892); Finch: J. Phys. Chem., **18**, 26 (1914).

[44] Mohanlal and Dhar: Z. anorg. Chem., **174**, 1 (1928).

[45] Löw: Z. anal. Chem., **9**, 463 (1870); Donath: **40**, 137 (1901).

[46] Müller: Z. physik. Chem., **105**, 73 (1923).

[47] Creighton: J. Am. Chem. Soc., **45**, 1237 (1923).

[48] Melbye: Chem. Abstracts, **17**, 1572 (1923); Jirsa: Kolloid-Z., **40**, 28 (1926).

[49] Z. anorg. Chem., **40**, 39 (1904); Chatterji and Dhar: Chem. News, **121**, 253 (1920).

a cobalt-blue crystalline cuprite from the alkali solution; so there is no doubt of the existence of such a salt. It is altogether probable that sol formation precedes cuprite formation when alkali acts on the gelatinous oxide.

The solubility of hydrous cupric hydroxide in alkali may be increased enormously by the presence of other substances. Thus, the addition of alkali to copper sulfate in the presence of tartrate forms the deep-blue solution known as Fehling's solution, so widely used in detecting small amounts of reducing sugar. The copper in this solution is present chiefly as a cupric tartrate complex[50] and not as cupric hydroxide sol. The same is generally true for the alkali solution formed in the presence of higher-valent alcohols, such as glycerol and mannitol, and of certain amines.[51] Gelatinous copper hydroxide is adsorbed strongly by hydrous chromic oxide, and the colloidal solution of the latter in alkali carries a considerable amount of the former into colloidal solution.[52]

CUPRIC OXIDE JELLIES

A cupric oxide jelly [43] forms on hydrolysis of a solution of cupric ammonium acetate of the formula $Cu(C_2H_3O_2)_2 \cdot 2NH_3$. It is unnecessary to start with this salt, and much more stable jellies are obtained by precipitation of a suitable amount of colloidal oxide at a suitable rate. The desired conditions may be realized by adding ammonia to cupric acetate in the presence of a small amount of sulfate and allowing the instable sol to precipitate spontaneously. The solution obtained is perfectly clear at the outset, but precipitation starts after intervals varying from a few seconds to several minutes depending on the relative amounts of the three components. In view of the great importance of rate of precipitation on jelly formation, the most favorable conditions are pretty sharply defined. A firm jelly that remains unbroken for weeks is obtained by mixing 5 cc of 3 N NH₄OH and 25 cc of 0.75 N Cu(C₂H₃O₂)₂ containing 2 cc of N K₂SO₄. The presence of sulfate is necessary in order to get a sol of sufficient concentration. Gelatinous precipitates instead of jellies are obtained by adding ammonia directly to copper sulfate, chloride, or nitrate, on account of the high velocity of precipitation.

[50] Küster: Z. Elektrochem., **4**, 112 (1897); Masson and Steele: J. Chem. Soc., **75**, 725 (1899); Kahlenberg: Z. physik. Chem., **17**, 577 (1895).

[51] Traube: Ber., **55B**, 1899 (1922); **56B**, 1653 (1923); Traube and Glaubitt: **63B**, 2094 (1930); Abegg: "Handbuch anorg. Chem.," **2** (1), 547 (1908).

[52] Cf. Knecht, Rawson, and Löwenthal: "A Manual of Dyeing," 241 (1916); Prud'homme: Bull. soc. chim. (2) **17**, 253 (1872).

HYDROUS CUPROUS OXIDE

YELLOW AND RED PRECIPITATED OXIDES

The yellow or orange precipitate thrown down from a cuprous salt solution by sodium hydroxide[53] or carbonate[54] is not CuOH but hydrous cuprous oxide so finely divided that it requires x-ray analytical methods to show that it is a definite crystalline form of the oxide which differs from the familiar red modification.[55] The yellow compound is best prepared by reduction of Cu^{++} in the presence of OH^- or by electrolysis of alkali salts in the cold with a copper anode.[56] For the chemical reduction, a variety of reducing agents may be used such as dextrose,[57] maltose,[58] and phenylhydrazine;[59] hydroxylamine hydrochloride[60] is particularly satisfactory. The yellow oxide is formed in the cold by the reduction of Fehling's solution with dextrose or in the hot when the amount of tartrate is too small to convert all the Cu^{++} into a complex. The clear yellow amorphous product goes over rapidly to an orange or reddish yellow color, probably with the loss of water. By drying in the absence of air, a stable product is obtained. This is changed to a brick-red powder by heating for 60 hours at 500°; and by igniting in a stream of nitrogen, it goes over to the familiar crystalline red form which is commonly obtained by reducing Fehling's solution at 100°. Similarly, the oxide formed by electrolyzing alkali salts is yellow at room temperature, bright red at 100°, and intermediate colors in between.[61] Red cuprous oxide is prepared on a commercial scale by electrolysis of a hot solution of sodium chloride with copper anodes.

The change in color of yellow hydrous cuprous oxide through orange and brick-red to bright red is not due to the change from one crystalline form into another but to an increase in particle size and loss of adsorbed water.[5] With this change, the reactivity with oxygen and the solubility in acids and alkalis fall off.

[53] Mitscherlich: J. prakt. Chem. (2) **19**, 450 (1840); Proust: J. phys., **51**, 182 (1800); Klason: Svensk Kem. Tid., **36**, 202 (1924).

[54] Fremy: Ann. chim. phys. (3) **23**, 391 (1848).

[55] Gröger: Z. anorg. Chem., **31**, 326 (1902); Moser: **105**, 112 (1919).

[56] Lorenz: Z. anorg. Chem., **12**, 438 (1896).

[57] Sandmeyer: Ber., **20**, 1494 (1887); Müller and Hagen: Pflügers Arch., **23**, 221 (1880).

[58] Glendinning: J. Chem. Soc., **67**, 999 (1895).

[59] Chattaway: Chem. News, **97**, 19 (1908).

[60] Moser: Z. anorg. Chem., **105**, 112 (1919); *cf.* Knoevenagel and Ebler: Ber., **35**, 3055 (1902).

[61] Miller: J. Phys. Chem., **13**, 256 (1909); Moser: Z. anorg. Chem., **105**, 112 (1919).

The colorless solution of hydrous cuprous oxide in ammonia turns blue in the air owing to the formation of $Cu(NH_3)_4^{++}$, thereby furnishing a delicate test for oxygen.

Red cuprous oxide is largely used in coloring glass red, a property known to the ancients and in the middle ages. The manufacture of this ancient red glass was revived by Bontemps in France and Englehardt in Germany about 1827. The oxide is also used for the production of a red glaze on pottery[62] and as a poisonous pigment in antifouling compositions for painting the bottoms of vessels.

CUPROUS OXIDE SOL

A sol of hydrous cuprous oxide is nearly always obtained in the reduction of alkali solutions of copper salts.[63] Similarly, during the reduction of cupric sulfate solution with stannous chloride[64] or hydrazine, yellow hydrous cuprous oxide[65] first appears, which goes over to the red oxide and finally to black copper sol. The reduction of a solution of copper tartrate with an ether solution of phosphorus gives a yellow-green sol which is fairly stable if not subjected to dialysis. The red oxide is readily peptized by concentrated ammonia or by ammonium sulfate in the presence of a small amount of ammonia.[66] Reduction of a neutral solution of copper sulfate in the presence of gum arabic or gelatin[67] gives a cuprous oxide sol which is stable in the absence of air. Gröger[68] obtained a stable sol on attempting to purify the orange hydrous oxide by prolonged washing in the absence of air.

HYDROUS COBALTOUS HYDROXIDE

COBALTOUS HYDROXIDE GEL

Formation and Composition

The addition of alkali to a solution of cobaltous salt gives a deep blue gelatinous precipitate which later changes to a rose color. Under certain conditions, the highly hydrous gel appears green rather than blue. X-ray analysis of the rose compound shows it to be $Co(OH)_2$

[62] Louth and Dutailly: Mon. Ceram. Verr., **19**, 237.

[63] *Cf*. Ruoss: Z. anal. Chem., **58**, 193 (1919).

[64] Lottermoser: J. prakt. Chem. (2) **59**, 492 (1899).

[65] Gutbier: Z. anorg. Chem., **32**, 355 (1902); Gutbier and Hofmeier: **44**, 227 (1905); *cf*. Paal and Leuze: Ber., **39**, 1550 (1906).

[66] Vuilleumier: J. Phys. Chem., **36**, 1455 (1932).

[67] Lobry de Bruyn: Rec. trav. chim., **19**, 236 (1900).

[68] Z. anorg. Chem., **31**, 326 (1902).

with a crystal structure similar to brucite, $Mg(OH)_2$.[69] Winkelblech[70] concluded that the blue gel is a basic salt and that oxidation is responsible for the green coloration which is frequently observed. The first conclusion was disproved by Hantzsch[71] and by Hüttig and Kassler,[72] who showed that both the blue and rose precipitates are cobaltous hydroxide. Hantzsch explained the difference in color by assuming that the blue is $CoO \cdot H_2O$, and the rose, $Co(OH)_2$. From x-ray diffraction studies, Stillwell[73] concluded that the difference in color between the blue and green compounds, on the one hand, and the rose, on the other, is due to isomerism, the former being the amorphous form and the latter the crystalline form of $Co(OH)_2$. From similar studies, Hüttig and Kassler claim that both the blue and rose compounds are crystalline and have the same crystal structure; the difference in color was attributed to particle size, the blue being the more finely divided. As we shall see, evidence obtained in the author's laboratory[74] indicates that the blue and rose compounds are two distinctly different crystalline forms of the hydroxide.

TABLE XIV

COLOR OF COBALT HYDROXIDES

(M $CoCl_2$ + 5 cc 2 M NaOH; total volume 25 cc)

M $CoCl_2$ cc	Color after				
	5 sec.	5 min.	1 day	3 days	8 days
5	Blue	Some rose	Rose	Rose	Rose
6	Blue	Light blue	Light blue	Light blue	Green blue
7	Blue	Green	Green	Green	Green
8	Blue	Green	Green	Green	Light blue
9	Blue	Green	Green	Green	Lavender
10	Blue	Green	Green	Light blue	Lavender
11	Blue	Green	Light blue	Lavender	Lavender
12	Blue	Some green	Light blue	Lavender	Lavender
13	Blue	Dark blue	Light blue	Lavender	Lavender
14	Blue	Dark blue	Some lavender	Lavender	Lavender

[69] Natta and Reina: Atti accad. Lincei (6) **4**, 51 (1926); Natta: Gazz. chim. ital. **58**, 355; Natta and Strada: 421 (1928).

[70] Ann., **13**, 155 (1835).

[71] Z. anorg. Chem., **73**, 304 (1912).

[72] Z. anorg. Chem., **187**, 16 (1930).

[73] J. Phys. Chem., **33**, 1247 (1929).

[74] Weiser and Milligan: J. Phys. Chem., **36**, 722 (1932).

Effect of Excess Cobalt Ion. If cobalt hydroxide is precipitated in the presence of a small excess of cobalt ion the transformation from blue to rose does not take place. This is shown by the observations recorded in Table XIV. The amounts of M $CoCl_2$ given in the first column were mixed with 5 cc of 2 M NaOH in a total volume of 25 cc. The experiments were carried out with air-free solutions and kept out of contact with air. It is apparent that a small excess of cobalt ion gives a permanent blue gel; a larger excess, a permanent green; and a still larger excess, a permanent lavender.
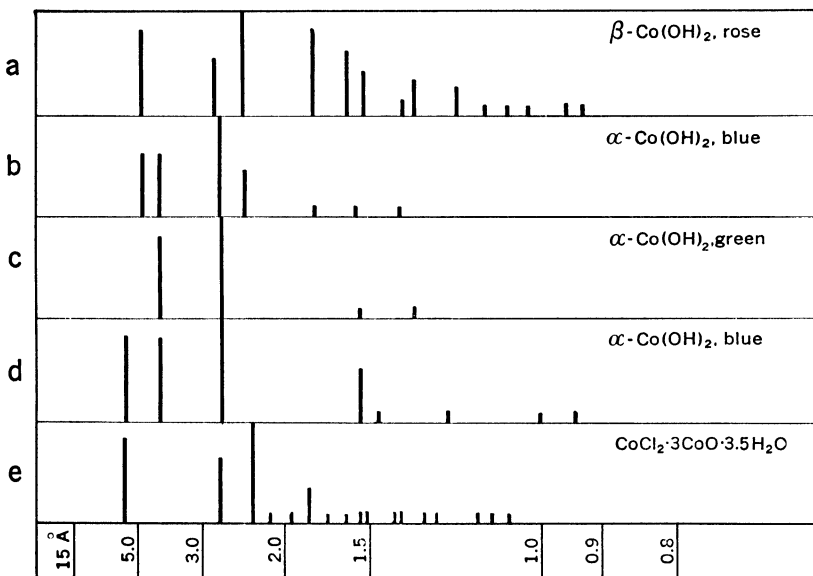
FIG. 28.—Diagrams of the x-ray diffraction patterns of cobalt hydroxides and basic chloride.

X-ray Analysis. Samples of the various colored products shown in Table XIV were prepared and subjected to x-ray analysis with the results shown in diagram form in Fig. 28. Sample a was thrown down in the cold with excess alkali, and after the transformation to rose was complete, it was washed with water until peptization started, then with alcohol, and finally dried at 60°; sample b was precipitated in the presence of a slight excess of cobalt chloride and dried like a; sample c was prepared like b but with a larger excess of cobalt chloride; sample d was precipitated in the presence of a small amount of mannitol, which greatly retards the blue-to-rose transformation; sample e

was an aged precipitate thrown down in the presence of a considerable excess of cobalt chloride.

Comparing the diagram of sample a which was the pure rose hydroxide with d which was almost pure blue, it will be seen that the two preparations are distinctly different in crystal structure. Since the patterns of samples b and d which were blue and sample c which was green are very similar, it seems altogether probable that the blue and green preparations are identical in crystal structure. The slight differences in the patterns of b, c, and d are due to the presence of varying small amounts of the rose compound mixed with the blue. Hüttig and Kassler probably had so much of the rose mixed with the blue that they failed to detect the differences in the x-ray pattern of the two preparations. The observed similarity in the dehydration isobars of the two hydroxides is accounted for by the fact that the blue form is transformed into the rose before the dehydration temperature is reached. According to Stillwell the blue and green preparations owe their difference in color to a difference in physical character. The green is the color by transmitted light, and the blue is a reflected color, a Tyndall blue.

The pattern of the violet preparation, Fig. 28e, is for the definite basic salt $CoCl_2 \cdot 3CoO \cdot 3.5H_2O$[75] and not for a hydroxide.

If we designate the blue and green preparations as α-$Co(OH)_2$ and the rose as β-$Co(OH)_2$, the color transformations and the composition of the various colored substances formed by the interaction of alkali and $CoCl_2$ may be represented as follows:

$$\left.\begin{array}{l}\alpha\text{-}Co(OH)_2;\ \beta\text{-}Co(OH)_2;\\ CoCl_2 \cdot 3CoO \cdot 3.5H_2O\\ \text{(green)}\end{array}\right\} \quad \underset{CoCl_2}{\overset{\text{Excess}}{\longleftarrow}} \quad \underset{\text{(blue,green)}}{\alpha\text{-}Co(OH)_2} \quad \underset{\text{alkali}}{\overset{\text{Excess}}{\longrightarrow}} \quad \underset{\text{(rose)}}{\beta\text{-}Co(OH)_2}$$

$$\downarrow$$

$$\left.\begin{array}{l}\alpha\text{-}Co(OH)_2;\ \beta\text{-}Co(OH)_2;\\ CoCl_2 \cdot 3CoO \cdot 3.5H_2O\\ \text{(blue)}\end{array}\right\} \quad \longrightarrow \quad \underset{\text{(lavender)}}{CoCl_2 \cdot 3CoO \cdot 3.5H_2O}$$
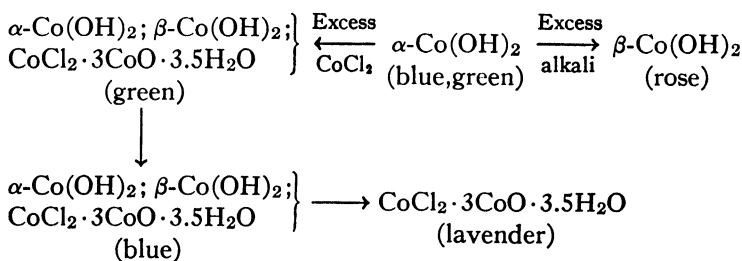
Stabilization of Blue Cobalt Hydroxide

From the observations recorded in the preceding section it appears that the blue cobalt hydroxide is stabilized by cobalt chloride, probably by its adsorption on the surface of the hydrous particles. Bene-

[75] Weiser and Milligan: J. Phys. Chem., **36**, 722 (1932); Stillwell: **33**, 1270 (1929); cf. Habermann: Monatsh., **5**, 445 (1884).

dict[76] showed that small amounts of nickelous hydroxide precipitated with the hydroxide retard the change in color from blue to rose. This stabilizing action, which appears to be specific,[9] is probably connected with the similarity in crystal structure of cobaltous and nickelous hydroxides.

Since the stabilization is probably the result of adsorption, a number of substances might be expected to retard or stop the change. It was found[74] that the blue form was stabilized for an indefinite period by small amounts of mannitol, sorbitol, dulcitol, sucrose,
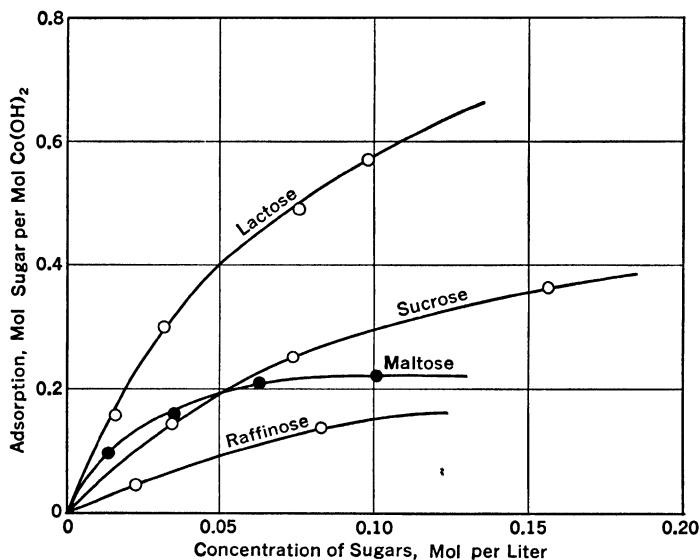
FIG. 29.—Adsorption of sugars by blue Co(OH)₂.

lactose, maltose, xylose, arabinose, raffinose, galactose, and dextrose, whereas the transformation was merely retarded by nickelous hydroxide, albumin, gelatin, and sulfates.

Adsorption of Sugars.   In view of the strong stabilizing action of sugars, one might expect them to be strongly adsorbed by the blue gel even at low concentrations.   That such is the case is evident from the adsorption studies shown in Fig. 29.[74]

Mechanism of the Transformation from Blue to Rose Cobaltous Hydroxide.   The probable mechanism of the transformation of the blue to rose hydroxide consists in the solution of the minute blue

[76] J. Am. Chem. Soc., **26**, 695 (1904); Test and Scoles: Proc. Indiana Acad. Sci., **34**, 163 (1924).

crystals in the excess alkali followed by reprecipitation of the less soluble, larger, rhombic crystals of the rose isomer. The addition of strongly adsorbed substances such as mannitol, various sugars, etc., surrounds the blue particles with a protecting layer which inhibits or prevents the isomeric transformation. In the presence of excess cobalt salt, the isomeric transformation is prevented not only by strong adsorption of the salt but also by the tendency to form a basic salt as described in the last section. In the absence of alkali, the solvent action of the mother liquor is insufficient to bring about the isomeric change, even at temperatures considerably above room temperature; on the other hand, in the presence of alkali, without the presence of a stabilizing substance, the transformation is quite rapid at higher temperatures.

COBALTOUS HYDROXIDE SOL

Cobaltous hydroxide may be peptized as a positive sol by thorough washing of the freshly formed gel.[77] The sol is quite dilute and relatively instable. The stability is increased but little by the addition of a small amount of dilute hydrochloric acid.[78]

Both blue and rose cobalt hydroxide dissolve in concentrated alkali, giving a solution with a deep-blue color. A similar color results on electrolyzing a solution of alkali, 4 N or stronger, with a cobalt anode. The blue solution was thought by Tubandt[79] to be colloidal cobalt oxide; but the results of exact potential measurements of cobalt against the blue solutions containing different amounts of cobalt in 8 N KOH, show conclusively that the blue color is due to potassium cobaltite, K_2CoO_2, and not to colloidal cobalt hydroxide.[80] Thus the behavior of cobalt hydroxide in excess alkali is similar to that of cupric hydroxide.

The sodium salts of lysalbinic and protalbinic acids[81] and glycogen[82] act as protecting colloids for the negative sol formed in the presence of dilute alkali. Under certain conditions, a part of the solution of cobalt hydroxide in dilute alkali is colloidal in the presence of sugar, glycerol, mannitol, and sodium tartrate.[83]

[77] Richards and Baxter: Proc. Am. Acad. Sci., **34**, 359 (1899); Tower and Cooke: J. Phys. Chem., **26**, 733 (1922); Stillwell: **33**, 1256 (1929).

[78] Müller: Z. anorg. Chem., **57**, 315 (1908).

[79] Z. anorg. Chem., **45**, 368 (1905); cf. Donath: Monatsh., **14**, 93 (1893).

[80] Grube and Feucht: Z. Elektrochem., **28**, 568 (1922).

[81] Paal and Boeters: Ber., **58B**, 1540 (1925).

[82] Hugounenq and Loiseleur: Compt. rend., **182**, 852 (1926).

[83] Dumanskii and Zaprometov: J. Russ. Phys.-Chem. Soc., **62**, 747 (1930); Sen and Dhar: Kolloid-Z., **33**, 194 (1923).

HYDROUS COBALTIC OXIDE

Cobaltic oxide in a highly hydrous state is precipitated on treating a solution of a cobaltous salt with alkaline hypochlorite,[84] alkaline persulfate,[85] alkaline permanganate,[86] or bromine, followed in each case by the addition of alkali.[87] It is also formed by electrolysis of an alkaline solution of cobalt sulfate[88] and by treating solutions of leuteo- and purpureo-cobalt chloride[89] or potassium cobalt cyanide or chloride with alkali. The gel is brownish black in color when mixed with some cobaltous hydroxide but is black when pure. Natta and Strada[90] made x-ray analysis studies on preparations obtained in various ways and of compositions varying between $Co_2O_3 \cdot 3H_2O$ and Co_2O_3. For every sample the x-ray pattern was the same, indicating that the gel is hydrous cobaltic oxide and that no hydrates are present. In opposition to this view, Hüttig and Kassler[89] observed a sudden vertical drop in the dehydration isobar of various samples when the composition is approximately $Co_2O_3 \cdot H_2O$ and the temperature is between 148 and 157°, depending on the method of precipitation of the sample. From these results the gel would appear to be hydrous monohydrate. It is not obvious why Natta and Strada failed to detect the existence of a monohydrate if one exists; and it is equally difficult to account for the form of the dehydration curves of Hüttig and Kassler in the absence of a monohydrate. The question can be settled only by further experimentation. Hüttig and Kassler claim that the hydrous compound starts to lose oxygen when the water content is below $1H_2O : 1Co_2O_3$ at a water vapor pressure of 10 mm of mercury; but Natta and Strada claim that the gel may be heated in the air up to 265° without losing oxygen.

Hydrous cobaltic oxide gel is peptized by thorough washing giving a sol which gradually precipitates on standing.[91]   A stable sol may

[84] Carnot: Compt. rend., **108**, 610 (1889); Schröder: J. Chem. Soc., **58**, 1213 (1890).

[85] Mawrow: Z. anorg. Chem., **24**, 263 (1900); Hüttner: **27**, 81 (1901); Dehn and Ballard: J. Am. Chem. Soc., **54**, 3264 (1932).

[86] Richards and Baxter: Proc. Am. Acad. Sci., **34**, 356 (1899).

[87] Fleischer: J. prakt. Chem. (2) **2**, 48 (1870); Jorissen: Z. anal. Chem., **21**, 209 (1882); Remmler: Z. anorg. Chem., **2**, 222 (1892).

[88] Coehn and Gläser: Z. anorg. Chem., **33**, 9; Coehn and Osaka: **34**, 86 (1903).

[89] Hüttig and Kassler: Z. anorg. Chem., **184**, 279 (1929).

[90] Gazz. chim. ital., **58**, 427 (1929); LeBlanc and Möbius: Z. physik. Chem., **A142**, 175 (1929); Merck and Wedekind: Z. anorg. Chem., **186**, 64 (1930).

[91] Hüttig and Kassler: Z. anorg. Chem., **184**, 281 (1929); Merck and Wedekind: **186**, 64 (1930).

be obtained by precipitating hydrous cobaltous hydroxide in the presence of the sodium salts of lysalbinic and protalbinic acids, followed by treating the resulting sol with hydrogen peroxide or allowing it to oxidize in the air.[81]

HYDROUS COBALTOUS-COBALTIC OXIDE

The gel of cobaltous-cobaltic oxide is obtained by oxidation in the air of hydrous cobaltous hydroxide[92] and by decomposition of hydrous cobaltic oxide by heating above 270°.[93]   The gel is also precipitated by heating aqueous solutions of cobalt amines.[94]   The x-ray diffraction pattern of the hydrous precipitate is the same as that for the anhydrous oxide.[93]   The crystal structure of the oxide is the same as that for the corresponding iron oxide, although the atomic distances in Co_3O_4 are somewhat smaller.[95]

A hydrous oxide whose oxygen content corresponds to that of a peroxide, CoO_2, is obtained by precipitating cobaltous hydroxide and oxidizing with an excess of iodine.[96]

HYDROUS NICKELOUS HYDROXIDE

The addition of potassium or sodium hydroxide to a solution of a nickelous salt throws down a voluminous apple-green precipitate[97] which was found to be $Ni(OH)_2$ by x-ray analysis.[98]   No hydrates of the hydroxide exist.   The purest preparation is obtained by using nickel nitrate or nickel ammonium nitrate rather than the sulfate or chloride, since nitrate ion is said to be least strongly adsorbed by the hydrous precipitate.[99]   The gelatinous oxide is readily soluble in ammonia, forming a deep-blue solution from which a green crystalline powder is precipitated by boiling.

To prepare the active form of $Ni(OH)_2$ for the Edison storage battery, the compound is precipitated from sulfate solution with an excess of sodium hydroxide.   The gel is dried slowly with the enclosed

[92] Fremy: J. prakt. Chem. (2) 57, 82 (1852); cf. Cross: J. Chem. Soc., 35, 797 (1879).

[93] Natta and Strada: Gazz. chim. ital., 58, 427 (1928).

[94] Gibbs and Genth: Am. J. Sci. (2) 23, 245 (1857); Lamb and Marden: J. Am. Chem. Soc., 33, 1882 (1911).

[95] Hendricks and Albrecht: Ber., 61B, 2153 (1928).

[96] Hüttner: Z. anorg. Chem., 27, 105 (1901); Vortmann: Ber., 24, 2744 (1891).

[97] Tower: J. Phys. Chem., 28, 176 (1924).

[98] Natta: Atti accad. Lincei (6) 2, 495 (1926); Gazz. chim. ital., 58, 344, 597 (1928); Cairns and Ott: J. Am. Chem. Soc., 55, 527 (1933).

[99] Bonsdorff: Z. anorg. Chem., 41, 136 (1904); Teichmann: Ann., 156, 17 (1870).

salts and alkali, which are subsequently washed out.   Excess of alkali increases the porosity of the product.[100]

A sol of nickel hydroxide results on mixing solutions containing equivalent amounts of nickel tartrate and potassium hydroxide. If the solutions are as concentrated as normal, precipitation takes place slowly, giving a transparent green jelly; but if the solutions are dilute, say $N/10$, a sol forms which can be purified by dialysis.[101] The alkali degradation products of albumin act as protecting colloids for this sol.[102]

The velocity of sedimentation of nickelous hydroxide depends on the concentration of the suspension.   The size of particles[103] as determined by the sedimentation velocity method corresponds with that obtained microscopically, only if the concentration is taken into account (Vol. I, p. 59).

HIGHER OXIDES OF NICKEL

The hydrous oxides of nickel having a valence higher than 2 are usually prepared by adding chlorine or bromine to a suspension of $Ni(OH)_2$ in alkaline solution or by warming a nickelous salt solution with basic solutions of such oxidizing agents as bromine, chlorine, and persulfates.   Bellucci and Clavari[104] made a series of preparations which were believed to be mixtures of hydrous NiO and NiO_2, by using different oxidizing agents at various temperatures.   The ratio of $Ni : O$ varied from $1 : 1.3$ to $1 : 1.9$, the latter ratio being obtained by carrying out the oxidation at $0°$.   By similar procedures, Clark, Asbury, and Wick[105] claimed to get $NiO_2 \cdot xH_2O$; Hüttig and Peter,[106] $Ni_2O_3 \cdot H_2O$; and Howell,[107] a mixture of hydrous Ni_2O_3 and NiO_2.   According to LeBlanc and Müller,[108] the black gel formed by oxidizing the freshly precipitated nickelous hydroxide with bromine contains 1 mol of nickel to approximately 1.75 mols of oxygen, of which 0.75 mol is active in the sense that it will oxidize hydriodic acid to iodine.   The preparation is instable even at room temperature,

[100] Edison: U. S. Pats. 1,083,355; 1,083,356 (1914); 1,167,484 (1916).

[101] Tower and Cooke: J. Phys. Chem., **26**, 728 (1922); Tower: **28**, 176 (1924).

[102] Paal and Brünjes: Ber., **47**, 2200 (1914).

[103] Tominaga: Bull. Inst. Phys. Chem. Research (Tokyo) **7**, 298 (1928).

[104] Gazz. chim. ital. **36**, 58 (1906); **37** (1), 409 (1907).

[105] J. Am. Chem. Soc., **47**, 2661 (1925); Pellini and Meneghini: Z. anorg. Chem., **60**, 178 (1908).

[106] Z. anorg. Chem., **189**, 190 (1930).

[107] J. Chem. Soc., **123**, 669, 1772 (1923).

[108] Z. Elektrochem., **39**, 204; cf. LeBlanc and Möbius: 753 (1933).

and acids drive off the oxygen until the Ni : O ratio is 1 : 1. Heating
the gel to 360° in vacuum drives off all the active oxygen and gives
gray-green NiO. In the isothermal dehydration of the hydrous
oxides no constant oxygen pressure and no constant water-vapor
pressure was observed. It was concluded therefore that there are no
definite higher oxides,[109] hydrous oxides, or hydrates of nickel.
Cairns and Ott,[110] on the other hand, obtained x-ray patterns of
preparations which appear to be higher hydrates. The gels formed
by adding nickelous nitrate solution to potassium hydroxide contain-
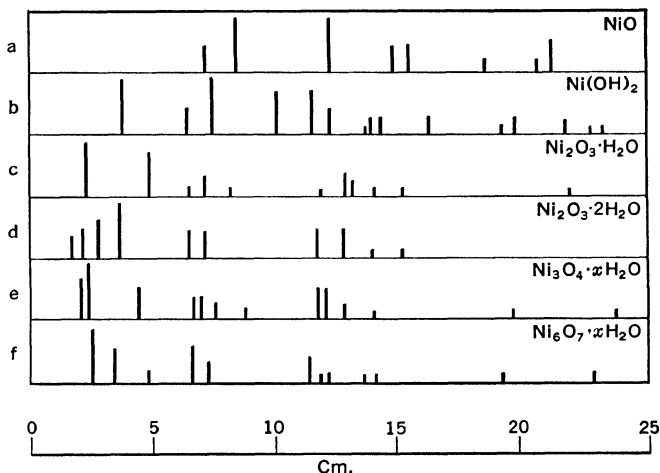
FIG. 30.—Diagrams of the x-ray diffraction patterns of nickel oxide and oxide hy-
drates. These diagrams show the linear distance in centimeters between correspond-
ing diffraction lines on opposite sides of the film. The dimensions of the camera were
such that this distance in millimeters was numerically equal to twice the angle
between incident and diffracted beams, measured in degrees.

ing bromine and that formed by adding the bromine solution to the
precipitated hydroxide give the same x-ray pattern as shown diagram-
matically in Fig. 30d. When the precipitate is dried for 3 days at
25° in a vacuum desiccator over calcium chloride, the composition is
approximately $Ni_2O_3 \cdot 2H_2O$ although the precipitate contains a small
amount of $Ni(OH)_2$. If an attempt is made to drive off more water
than corresponds to $2H_2O$, by heating to 130° for 24 hours, oxygen

[109] LeBlanc and Sachse: Z. Elektrochem., **32**, 59, 204 (1926); Hendricks, Jefferson,
and Schultz: Z. Kryst., **73**, 376 (1930).
    [110] J. Am. Chem. Soc., **55**, 534 (1933); **56**, 1094 (1934); Z. Elektrochem., **40**, 286
(1934); cf. Goralevich: J. Gen. Chem. (U.S.S.R.) **1**, 973 (1931).

is lost and the x-radiogram for NiO, Fig. 30a, is obtained. By heating the so-called $Ni_2O_3 \cdot 2H_2O$ in water in a bomb tube at 150°, $Ni(OH)_2$ is formed, which gives the x-ray pattern shown diagrammatically in Fig. 30b. If the original gel is precipitated at 100° instead of at room temperature, the product approaches the composition Ni_3O_4 with varying water content and gives the x-ray pattern, the diagram of which is shown in Fig. 30e. If a sample which gives the diagram e is heated for 4 hours at 110° in the air, it has the composition $Ni_6O_7 \cdot xH_2O$ and gives the pattern shown diagrammatically in Fig. 30f. By further oxidation of $Ni_3O_4 \cdot xH_2O$ with bromine in alkali, hydrous $Ni_2O_3 \cdot H_2O$ is said to form which gives the x-radiogram c, Fig. 30. The alleged compounds are believed to contain the water bound as hydroxyl groups rather than as H_2O.

As already pointed out, dehydration and decomposition experiments carried out by LeBlanc and his students argue against the presence of higher oxides; but LeBlanc and Möbius admit the existence of interference lines which are not due to cubic NiO or rhombohedral $Ni(OH)_2$, in Cairns and Ott's x-ray patterns. It is suggested that these may be caused by the presence of some hydrate of NiO or of $Ni(OH)_2$ rather than of higher oxides; but there is no experimental justification for the suggestion. Further work will be necessary before it is possible to reconcile the views of Cairns and Ott and of LeBlanc.

The black hydrous oxide of nickel is peptized by small amounts of organic acids, such as acetic, citric, and tartaric, forming a very stable sol. Peptization results on washing the hydrous oxide with cold water, but the sol obtained in this way is not stable.[111]

HYDROUS SILVER OXIDE

By mixing a dilute solution of silver nitrate and potassium hydroxide in 90% alcohol at −45°, hydrous silver oxide comes down as a flocculent mass almost pure white in color.[112] As the temperature rises, it changes in color from pale brown to brown, owing to loss of adsorbed water and agglomeration of the particles. The hydrous oxide precipitated at room temperature is brown, but becomes black on drying at temperatures as low as 50 to 65°. Pure silver oxide decomposes slightly even at 100°,[113] and it does not give up all its adsorbed water until a temperature of 280° is reached; accordingly,

[111] Tubandt and Riedel: Z. anorg. Chem., **72**, 219 (1911).
[112] Bruce: Chem. News, **50**, 208 (1884).
[113] Rose: Pogg. Ann., **85**, 314 (1852).

pure silver oxide cannot be obtained.[114] Riley[115] claims that silver hydroxide exists as a surface film on the oxide dried to 0.3% H_2O.

A silver oxide sol is formed both by heating silver wire to redness and plunging it suddenly into water,[116] and by mixing $N/40$ $AgNO_3$ with a slight excess of KOH of similar concentration.[117] A stable sol is obtained only when the hydrous oxide is precipitated in the presence of a protecting colloid such as glycogen,[118] tannin,[119] or Paal's sodium protalbinate or lysalbinate.[120] A saturated solution of silver oxide usually contains a trace of the highly dispersed oxide unless the solution is ultrafiltered.[121]

· THE HYDROUS OXIDES OF GOLD

Hydrous Auric Oxide. The hydrous oxide formed by treating auric chloride with alkali or by decomposing potassium aurate with acid is always contaminated with adsorbed alkali or salt which cannot be removed by washing.[122] It may be obtained pure by heating a solution of gold chloride with magnesia and decomposing the residue with nitric acid.[123] The hydrous oxide is yellow or olive green, depending on the method of formation, and becomes brown to black on drying. A sample precipitated from potassium aurate with acid contained more than $8H_2O$ to $1Au_2O_3$;[124] and one thrown down from the chloride solution with barium hydroxide approached the composition $Au_2O_3 \cdot 3H_2O$[125] when dried in vacuum over calcium chloride, and $Au_2O_3 \cdot H_2O$[126] when dried over phosphorus pentoxide. These data offer no proof of the existence of a definite hydrate, and it is altogether likely that none is formed. Like hydrous silver oxide, the gold

[114] Madsen: Z. anorg. Chem., **79**, 200 (1913); Hardin: J. Am. Chem. Soc., **18, 994** (1896); Lea: Am. J. Sci. (3) **44**, 249 (1892).

[115] Phil. Mag. (7) **3**, 459 (1927).

[116] Kimura: Mem. Coll. Sci. Eng., Kyoto Imp. Univ., **5**, 211 (1913).

[117] Lottermoser: J. prakt. Chem. (2) **72**, 39 (1905); Ghosh and Dhar: J. Phys. Chem., **30**, 294 (1926).

[118] Hugounenq and Loiseleur: Compt. rend., **182**, 851 (1926).

[119] Sensburg: German Pat. 208,189 (1907).

[120] Paal and Voss: Ber., **37**, 3862 (1904); Lottermoser: J. prakt. Chem. (2) **71**, 296 (1905).

[121] Weiser and Roy: J. Phys. Chem., **37**, 1009 (1933).

[122] Schottländer: Ann., **217**, 312 (1883).

[123] Pelletier: Ann. chim. phys. (2) **15**, 113 (1820); Lenher: J. Am. Chem. Soc., **25**, 1137 (1903); Morris: **40**, 917 (1918).

[124] Figuier: Ann. chim. phys. (3) **11**, 336 (1844).

[125] Wittstein: Pharm. Vierteljahr, **15**, 51 (1866).

[126] Krüss: Ber., **19**, 2541 (1886).

compound decomposes below the temperature at which all the adsorbed water can be driven off.   At 160° a composition corresponding to the formula, Au_2O_2, gold dioxide,[127] has been obtained, but the identity of such a compound has not been established.

Hydrous Aurous Oxide.   If a solution of an aurous salt[128] is treated with potassium hydroxide, a dark-violet precipitate results, which is said to be aurous hydroxide; but there is no evidence to support this view, and it is probably Au_2O with adsorbed water.   A similar product is obtained by hydrolysis of an aurous salt[122] or by reduction of an auric salt with mercurous nitrate.[129]   The hydrous oxide appears to give up all its adsorbed water at 200°, and oxygen is not evolved until a somewhat higher temperature.   The freshly precipitated and washed gel is peptized by shaking with water,[130] forming a fairly stable indigo-blue sol with a brown fluorescence.[131]   The sol shows an absorption maximum between λ = 586.5 and 597.5,[132] whereas the absorption maximum for colloidal gold is at λ = 535.   By boiling the sol or by allowing it to stand several days, the dark-violet hydrous oxide is precipitated.   The stability of the sol would probably be increased by more thorough washing, preferably with a centrifuge, before shaking with water.

[127] Krüss: Ber., **19**, 2541 (1886); Dudley: Am. Chem. J., **28**, 61 (1902).

[128] Berzelius: Jahresber., 199 (1848); Krüss: Ann., **237**, 274 (1887); Prat: Compt. rend., **70**, 840 (1870).

[129] Figuier: Ann. chim. phys. (3) **11**, 336 (1844).

[130] Krüss: Ber., **19**, 2541 (1886); Ann., **237**, 274 (1887).

[131] Vanino: Ber., **38**, 462 (1905).

[132] Vogel: "Die prakt. Spektralanalyse iridischer Stoffe," Berlin, **1**, 489 (1889).

CHAPTER VI

THE HYDROUS OXIDES AND HYDROXIDES OF BERYLLIUM, MAGNESIUM, ZINC, CADMIUM, AND MERCURY

HYDROUS BERYLLIUM HYDROXIDE

GELATINOUS BERYLLIUM HYDROXIDES

Hydrous beryllium hydroxide is thrown down in a gelatinous condition resembling hydrous alumina preferably by the addition of ammonia to an aqueous solution of a beryllium salt. It is also obtained by conducting carbon dioxide rapidly into a 1% solution of the hydroxide in 4% NaOH.[1] In this form it possesses such a high adsorption capacity that it cannot be washed free from salt adsorbed from the mother liquor. The washing must be carried out in the absence of carbon dioxide since the freshly formed gel will take up as much as one-third of an equivalent of the gas.[2] The gel may be freed almost completely from adsorbed sulfate and carbonate by electrodialysis in a three-cell dialyzer between thick collodion membranes.[3]

The freshly formed gel gives no x-ray diffraction pattern, but on washing and aging under water it may give a definite pattern in the course of a few days. Thus, a gel thrown down from the sulfate and purified by electrodialysis gave a good pattern in less than a month, whereas a precipitate from the nitrate which was not purified by electrodialysis gave no pattern after 2 months.[4]

It is commonly stated that the gel precipitated in the cold is amorphous and is transformed into a definitely crystalline form by aging. This may be true, but the possibility has not been excluded that the freshly formed gel is composed of crystals too small to diffract the x-rays. Havestadt and Fricke claim that the appearance of definite

[1] Havestadt and Fricke: Z. anorg. Chem., **188**, 357 (1930).
[2] Haber and van Oordt: Z. anorg. Chem., **38**, 380 (1904).
[3] Fricke: Kolloid-Z., **49**, 229 (1929).
[4] Havestadt and Fricke: Z. anorg. Chem., **188**, 357 (1930); Fricke and Lüke: Z. physik. Chem., **B23**, 319 (1933); *cf.* Böhm and Niclassen: Z. anorg. Chem., **132**, 1 (1924).

crystals manifests itself by an increase in the dielectric constant of the gel.

The water content of the hydroxide is indefinite, depending on the temperature and vapor pressure of the surrounding air.[5]   The various hydrated beryllium hydroxides described by Atterberg[6] and others[7] merely represent different stages in the removal of adsorbed water from a hydrous hydroxide.

The fresh gel is readily dissolved by dilute acids, alkalis, and ammonium carbonate and alkali carbonate as well as by solutions of beryllium salts.   The great solubility of the gel in sodium bicarbonate serves to distinguish beryllium and to separate it quantitatively from iron and aluminum.[8]   Like most hydrous precipitates, the adsorbability and solubility of beryllium hydroxides decrease slowly on standing at room temperature and more rapidly at higher temperatures.   The aging manifests itself not only by a marked diminution in specific surface but also by the appearance of crystals sufficiently large to give a well-defined x-ray diffraction pattern.

Concentrated solutions of normal beryllium salts can dissolve 2 to 6 equivalents of hydrous beryllium hydroxide; thus, the oxalate or sulfate dissolves nearly 3 equivalents, the chloride 4, and the acetate nearly 6.   In every case the hydrous oxide precipitates on dilution, although the precipitation is not complete.   This solution is not due to the formation of a molecular complex, nor is there any evidence of sol formation.[9]   Parsons[10] believes that the dissolved beryllium salt merely acts as a solvent for hydrous beryllium oxide just as an aqueous solution of acetic acid dissolves camphor which is itself insoluble in water.

If hydrous beryllium oxide is precipitated in the presence of boric acid, the distribution of the latter between the hydrous oxide and water is independent of the concentration of boric acid, both at 20 and 100°.   Similarly, the composition of the precipitate formed by mixing sodium borate and beryllium sulfate varies with the concentration and the relative proportion of the reacting substances.   It is evident, therefore, that the so-called beryllium borates,[11] like a large number

   [5] Van Bemmelen: J. prakt. Chem. (2) **26**, 227 (1882); Hüttig and Toischer: Z. anorg. Chem., **190**, 364 (1930).

   [6] Köngl. Svenska Vet. Akad. Hand., **12**, 1 (1873).

   [7] Bleyer and Kaufmann: Z. anorg. Chem., **82**, 71 (1913).

   [8] Parsons: "The Chemistry of Beryllium," 9, 27 (1908).

   [9] Parsons, Robinson, and Fuller: J. Phys. Chem., **11**, 651 (1907).

   [10] J. Phys. Chem., **11**, 659 (1907).

   [11] Bleyer and Paczuski: Kolloid-Z., **14**, 295 (1914).

of alleged beryllium compounds,[12] are, in reality, solid solutions of boric acid and hydrous beryllium oxide.[13] Arsenious oxide likewise seems to form solid solutions with beryllium oxide at 100°, but at room temperature, the acid is adsorbed by the gel, giving a well-defined adsorption isotherm.[14] A freshly formed hydrous oxide adsorbs[15] acid dyes, such as eosin and Congo red, the latter being taken up more strongly than by hydrous alumina. It also adsorbs invertin and amylase more strongly than alumina. Basic dyes, such as methylene blue, are adsorbed very slightly, and the same is true for acetic acid, grape sugar, and tributyrin. The adsorption capacity of gels decreases rapidly with age on account of the rapid change from a gelatinous to a granular structure. The rapidity with which the highly adsorptive gel goes over into a slightly adsorptive state, particularly at 100°, may account for Prud'homme's[16] observation that beryllium hydroxide does not act as a mordant.

GRANULAR BERYLLIUM HYDROXIDES

The granular crystalline hydroxide which forms slowly when the gel is allowed to age in contact with water,[1] and more rapidly in contact with a solution of ammonia,[17] is designated α-Be(OH)$_2$. This is the metastable form of the hydroxide which goes over spontaneously to the stable β-hydroxide by shaking with alkali. The stable form is also obtained when a saturated solution of beryllium hydroxide in hot 40% NaOH is allowed to cool slowly,[18] or when the cold, saturated solution is allowed to stand for several days in a closed flask.

Beryllium hydroxide possesses a slight acidic character[19] and forms beryllates with alkalis. The salts, Be(OK)$_2$ and Be(ONa)$_2$, have been obtained in a crystalline form from alcoholic solutions,[20] and BeO·NaOH·H$_2$O from concentrated sodium hydroxide solution.[21]

[12] Parsons: "The Chemistry of Beryllium," 69 (1908).

[13] Krüss and Moraht: Ber., **23**, 727 (1890).

[14] Bleyer and Müller: Arch. pharm., **251**, 304 (1913); Z. anorg. Chem., **75**, 285 (1912).

[15] Kleeberg: Kolloid-Z., **37**, 17 (1925).

[16] Bull. soc. chim. (3) **13**, 509 (1895).

[17] Haber and van Oordt: Z. anorg. Chem., **38**, 377 (1904); Fricke and Humme: **178**, 400 (1929).

[18] Fricke: Z. anorg. Chem., **166**, 245 (1927); Fricke and Humme: **178**, 400 (1929); Hüttig and Toischer: **190**, 364 (1930).

[19] Hantzsch: Z. anorg. Chem., **30**, 289 (1902); Ley: Z. physik. Chem., **30**, 218 (1899); Bleyer and Kaufmann: **82**, 80 (1913).

[20] Krüss and Moraht: Ann., **260**, 173 (1890).

[21] Fricke and Humme: Z. anorg. Chem., **178**, 400 (1929).

About 40% of an aqueous solution of the sodium salt is hydrolyzed in a 0.1 N solution.[22]   According to Hantzsch the solution of hydrous beryllia in alkali is only partly beryllate.   From a concentrated solution, $Be(OH)_2$ precipitates spontaneously on standing for a long time or rapidly on heating.   It seems likely that the first step in the solution process is peptization by preferential adsorption of hydroxyl ion. This is followed by the formation of beryllate, the breaking down of which gives granular crystals of the difficultly soluble crystalline hydroxide.   As Ostwald[23] points out, the stable hydroxide is not present in the original solution, which soon becomes supersaturated with respect to it; but precipitation can commence only after the first
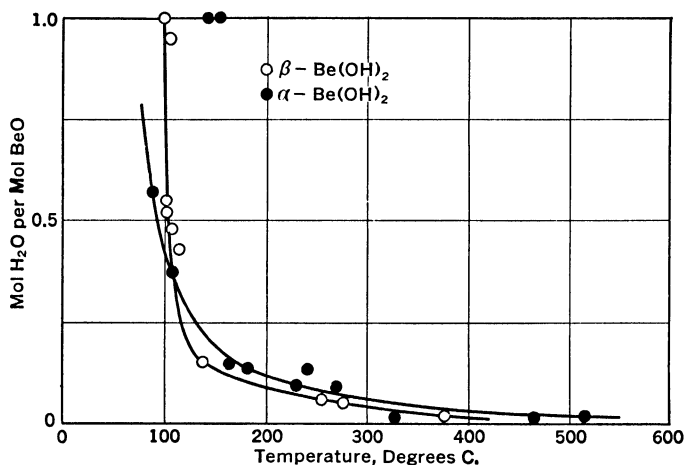
FIG. 31.—Dehydration isobars of α-Be(OH)₂ and β-Be(OH)₂.

traces have come down, a step that occurs slowly at ordinary temperatures, but rapidly when the solution is heated.   Unlike alumina, hydrous beryllium hydroxide is neither peptized nor dissolved by ammonia[24] nor by methyl- or ethylamine.[25]

The α- and β-hydroxides give distinctly different x-radiograms. Dehydration isobars of the two isomers, as obtained by the precise procedure of Fricke and Severin[26] (p. 92), are shown in Fig. 31. The decomposition temperature of the β-hydroxide is 105° at a water-

[22] Wood: J. Chem. Soc., **97**, 878 (1910).
[23] "The Principles of Inorganic Chemistry," London, 546 (1902).
[24] Weeren: Pogg. Ann., **92**, 91 (1854).
[25] Renz: Ber., **36**, 2751 (1903).
[26] Z. anorg. Chem., **205**, 287 (1932).

vapor pressure of 100 mm of mercury. The metastable α-hydroxide does not have a definite decomposition temperature, but at a composition $BeO \cdot 0.5H_2O$ it is approximately 95°. For the corresponding hydroxides, Hüttig and Toischer[27] observed the decomposition temperatures 188 and 184°, respectively, at a water-vapor pressure of 10 mm of mercury. The higher values obtained by the latter investigators are probably due to the limitations of their experimental procedure and to the use of impure preparations.

The molecular heat of formation of the metastable hydroxide in hydrofluoric acid is 22.5 Cal. and that of the stable hydroxide 21.6 Cal.[28]

BERYLLIA SOL

Since freshly formed beryllium hydroxide loses its hydrous character and becomes definitely crystalline in a relatively short time, stable concentrated sols of the compound have not been prepared. Böhm and Niclassen[29] obtained a fairly concentrated sol by peptizing the newly formed gel with 0.05 N HCl, but most of the colloidal material in such sols settles out in a few days. Since the gelatinous hydroxide runs through the filter paper when an attempt is made to wash out adsorbed salts, sols may be prepared by thorough washing of the hydrous gel. In this case, also, the colloidal material settles out in a short time.

Madson and Krauskopf[30] obtained dilute but stable sols in the following way: Pure basic beryllium acetate was converted into the chloride by boiling a small amount of the former with 6 N HCl. After evaporating to a syrupy consistency, a 15-cc portion was heated in a 6-inch casserole until nearly dry, after which the residue was heated with the full flame until the redness of the flame could be seen through the bottom of the casserole. At this point, 1 l of boiling water was added and the resulting sol was boiled for a minute and allowed to cool. The stability of the sol is indicated by the fact that one preparation contained 193 mg BeO per l at first and 178 mg after one year. Purification by dialysis in the hot for several days reduced the concentration below 100 mg per l, and the pH value of the sol increased from 5.6 to 7.0. The size of the particles was found to be approxi-

[27] Z. anorg. Chem., **190**, 364 (1930); *cf.* Hackspill and Kieffer: Ann. chim. (10) **14**, 227 (1930).

[28] Fricke and Wullhorst: Z. anorg. Chem., **205**, 127 (1932).

[29] Z. anorg. Chem., **132**, 1 (1924).

[30] J. Phys. Chem., **35**, 3237 (1931); Madson: Trans. Ill. Acad. Sci., **25**, 171 (1933).

mately 150 mμ for the cube edge.[31]   The particles were not beryllium hydroxide but hydrous BeO which had adsorbed less than one-half the amount of water corresponding to Be(OH)$_2$.

The positively charged beryllium oxide sol behaves like a dilute hydrophobic sol toward electrolytes.   A summary of the precipitation values is given in Table XV.   The order of precipitating power of the

TABLE XV

PRECIPITATION VALUES OF ELECTROLYTES FOR Be(OH)$_2$ SOL

(Millimols per liter)

Electrolyte	Precipitation value	Electrolyte	Precipitation value
KCl..................	227	K$_2$SO$_4$...............	0.211
CH$_2$ClCOOK.........	143	Na$_2$SO$_4$..............	0.200
CHCl$_2$COOK..........	81	K$_3$PO$_4$...............	0.048
CCl$_3$COOK...........	73	KH$_2$PO$_4$.............	0.046
CH$_3$COOK...........	59	K$_3$AsO$_4$..............	0.044
K$_2$CrO$_4$..............	0.229	K$_2$HPO$_4$·3H$_2$O........	0.033
MgSO$_4$...............	0.220	K$_3$Fe(CN)$_6$...........	0.025
(NH$_4$)$_2$SO$_4$............	0.213	K$_4$Fe(CN)$_6$...........	0.010

several electrolytes is, in general, what would be expected from similar observations on other sols.   The order for the several phosphates cannot be accounted for simply from the standpoint of ionization and adsorption.   It is suggested that sols of the amphoteric type like beryllia may have a minimum of stability at some rather definite pH value of the system.   The order of decreasing flocculating power of the several acetates in the series: CH$_3$COO$^-$ > CCl$_3$COO$^-$ > CHCl$_2$COO$^-$ > CH$_2$ClCOO$^-$, would not be deduced from the order of (1) increasing degree of dissociations of the acids, (2) increasing molar conductances of the salt, (3) increasing ionic mobilities of the acetate ions. Moreover, the variation in the conductances and in the ionic mobilities is insufficient to account for the large variation among the precipitation values in the series.   Apparently the precipitating power is determined by the extent of ionization, the adsorbability, and the size of the ions, which in turn influences the adsorbability.

[31] Madson: J. Phys. Chem., **36**, 855 (1932).

HYDROUS MAGNESIUM HYDROXIDE

PRECIPITATED MAGNESIA

Magnesium hydroxide in a flocculent hydrous condition is formed by the action of water on magnesia obtained from the naturally occurring carbonate, magnesia alba.[32] It is also thrown down by the addition of alkali or ammonia to a solution of magnesium salt when the pH value reaches 10.4.[33] This pH value is not obtained with ammonia in the presence of excess ammonium chloride, and the precipitation is prevented. When the precipitation is made with alkali the latter is adsorbed so strongly[34] that its presence prevents the adsorption of sulfate and chloride.[35]

The freshly precipitated hydroxide is more soluble than the aged precipitate.[36] This is probably due to the difference in particle size, since Fricke[37] showed that fresh and aged precipitates give the same x-radiogram. However, the fresh preparation gives a pattern with weaker and broader lines than the aged, as would be expected if the crystals of the former are smaller. X-ray analysis of the precipitate shows it to be a true hydroxide indentical with natural brucite.[38] Large crystals of the hydroxide may be prepared by heating magnesium chloride with an excess of potash in a limited amount of water.[39]

A jelly of magnesium hydroxide is obtained by adding a small amount of water to a 3% solution of magnesium methylate in methyl alcohol.[40] The jelly is not very stable and synerizes rapidly, the more readily the higher the concentration. The jelly may be stabilized by the addition of such substances as glycerol or glycol, probably owing to their peptizing action. By using water, glycerol, and alcohol in the ratio 5 : 10 : 10, a plastic, glass-clear jelly is obtained which is stable for months. The superior quality of the preparation is probably due to the fact that thorough mixing of the ingredients can be accomplished before the jelly starts to form (p. 15). Small amounts of potassium

[32] Deville: Compt. rend., **61**, 975 (1865); Ditte: **73**, 191 (1871).

[33] Britton: J. Chem. Soc., **127**, 2110 (1925).

[34] Grouvelle: Ann. chim. phys. (2) **17**, 354 (1821); Marchand and Scheerer: J. prakt. Chem., **50**, 385 (1850).

[35] Patten: J. Am. Chem. Soc., **25**, 186 (1903).

[36] Gjaldbaek: Z. anorg. Chem., **144**, 145, 269 (1925).

[37] Z. anorg. Chem., **166**, 244 (1927).

[38] Böhm and Niclassen: Z. anorg. Chem., **132**, 6 (1924); Levi and Ferrari: Atti accad. Lincei (5) **33** I, 397 (1924); Natta: Gazz. chim. ital., **58**, 344, 597 (1928).

[39] De Schulten: Compt. rend., **101**, 72 (1885).

[40] Kröger and Fischer: Kolloid-Z., **47**, 5 (1929).

hydroxide increase the rate of formation of the jelly, but larger amounts throw down a gelatinous precipitate.

If powdered magnesium is brought in contact with mercury under water, a concentrated magnesium hydroxide sol results which coagulates spontaneously, giving a jelly.[41]

Rhythmic Precipitation

Magnesium hydroxide may be precipitated in gelatin jelly in the form of broad, sharply defined rhythmic bands or Liesegang rings. By allowing strong ammonia to diffuse into gelatin containing magnesium chloride, Popp[42] found that, with increasing concentration of magnesium salt, the rings increase in number and thickness, and the space between them decreases; with diminishing ammonia concentration, the rings decrease in number and thickness, and the space between them increases; adding ammonium chloride causes the number and thickness of the rings to decrease and the space between them to increase; with diminishing gelatin concentration, both the rings and the space between them increase, the number remaining the same. The rhythmic precipitation takes place also in clay, agar, silica gel, fine sand, and glass beads in water. To account for these and other Liesegang phenomena, Wolfgang Ostwald[43] postulates the existence of three principal diffusion waves in all reacting systems giving typical periodic precipitates: the added electrolyte diffuses into the gel; the electrolyte in the gel diffuses outward; and the electrolyte produced by the reaction may diffuse in both directions. In many instances the soluble reaction product possesses a higher rate of diffusion than one or both of the reactants. Ostwald assumes, further, that many and probably all reactions giving Liesegang rings are balanced reactions. Precipitation, therefore, depends on certain critical concentrations of reactants which vary over wide ranges through the interference of diffusion waves. In support of the theory, it was shown that many Liesegang rings are destroyed by subsequent introduction, by diffusion, of the electrolyte produced in the reaction. Thus, bands of magnesium hydroxide are destroyed by allowing ammonium chloride to diffuse into the gel supporting them. The converse of rhythmic precipitation, namely rhythmic solution, may sometimes be produced by adding a reaction product. Thus, a uniform precipitate of lead sulfate in gelatin gel containing ammonia is converted into

[41] Jakovlev: J. Russ. Phys.-Chem. Soc., **60**, 1551 (1928).

[42] Kolloid-Z., **36**, 208 (1925).

[43] Kolloid-Z. (Zsigmondy Festschrift) **36**, 380 (1925).

rings by the interdiffusion of concentrated ammonium chloride. Continuous precipitation results if one reactant is replaced by a compound not giving a balanced reaction, as evidenced by the failure to get bands when alkali is substituted for ammonia in the precipitation of magnesium hydroxide in gelatin. The distribution of chloride ions in a gelatin jelly containing magnesium chloride was found, after the diffusion of ammonia, to show periodic variation between values much higher and much lower than those of the original gel.

Wolfgang Ostwald's "diffusion wave" theory of rhythmic banding considers as secondary to the banding process such phenomena as supersaturation,[44] peptization and coagulation of the precipitate,[45] adsorption of reacting solutes by the precipitate,[46] etc. (p. 24). It has been developed largely on the magnesium hydroxide system and is admittedly applicable only to the rhythmic structures formed by chemical reactions which are associated with the three diffusion waves above mentioned. Although the theory may represent the mechanism of the banding process in certain systems, it is not general. Thus Hedges and Henley[47] prepared colloidal magnesium hydroxide by mixing equivalent amounts of magnesium chloride and ammonia in 6.5% gelatin and allowing the mixture to set in test tubes, after which ammonia was poured over the jelly. Rhythmic bands were obtained comparable with those produced by direct diffusion of ammonia into gelatin containing magnesium chloride alone. Similar observations were made with silver dichromate in gelatin and with lead iodide in agar. From these experiments it would appear that the formation of the banded structures is a coagulation phenomenon taking place after the chemical reaction is completed. In any event, the diffusion waves postulated by Ostwald are not essential to the process. Moreover, Hedges and Henley point out that the diffusion-wave theory fails completely in explaining the rhythmic structures formed when potassium iodide or lead nitrate diffuses into lead iodide dispersed in agar. In this case, the greatest possible number of diffusion waves that can be set up is two, and yet the resulting bands are essentially the same as those formed by chemical interaction of lead nitrate and potassium iodide in agar.

By analysis of the bands and the clear spaces in a magnesium

[44] Ostwald: "Lehrbuch allgem. Chemie," 2nd ed., 2, 778 (1911).

[45] Freundlich: "Kapillarchemie," 2nd ed., 1009 (1922); Sen and Dhar: Kolloid-Z., 34, 270 (1924).

[46] Bradford: Biochem. J., 10, 169 (1916).

[47] J. Chem. Soc., 2714 (1928); Hedges: 2779 (1929); Kolloid-Z., 52, 219 (1930).

hydroxide system, Hedges and Henley showed that the ratio of magnesium hydroxide in the bands to that in the clear spaces was 12 : 1; and the corresponding ratio for ammonium chloride was 1 : 3.[48]

Applications

Hydrous magnesium hydroxide has been suggested as a substitute for charcoal as a clarifier in the refining of sugar.[49] In the petroleum industry it may be used in a granular form in place of alkali to remove phenols, acid remaining after acid treatment, and hydrogen sulfide; and as a sweetening agent under suitable conditions.[50]

The mild basic action of magnesium hydroxide has been utilized in pharmaceutical preparations as an antacid. Milk of magnesia is a fairly stable suspension of the hydrous oxide that is widely employed as a mouth wash, in the preparation of modified milk for infants, and in combating hyperacidity of the stomach. The colloidal hydroxide appears to have a very definite therapeutic action when injected intravenously in the treatment of toxic hepatitis and nephritis.[51] The precipitated hydroxide is an antidote to mercuric chloride poisoning but is much less effective than carbon.[52] It is quite effective in removing diphtheria toxin from toxic broth.[53]

HYDRATION OF MAGNESIA

Like calcium oxide, magnesia takes up water, re-forming magnesium hydroxide under suitable conditions. In general, the rate at which water is taken up decreases with increasing ignition temperature, the anhydrous oxide obtained at high temperatures hydrating very slowly. Campbell[54] burned magnesite between 600 and 800°, obtaining an impure oxide which hydrates completely in 3 days. Between 1000 and 1100°, the magnesia was said to undergo a change resulting in a marked decrease in the rate of hydration until at 1450°, about the temperature used in burning Portland cement, the oxide, immersed in water for 18 months, combined with 60% of that necessary to form $Mg(OH)_2$. Le Chatelier[55] gave 1600° as the transformation tem-

[48] *Cf., also,* Fricke and Suwelack: Z. physik. Chem., **124**, 359 (1926).

[49] Hake: J. Soc. Chem. Ind., **2**, 149 (1883).

[50] Gardner and Higgins: Ind. Eng. Chem., **24**, 1141 (1932).

[51] Pribyl: Chem. Abstracts, **23**, 3985 (1929); Arch. exptl. Path. Pharmakol., **160**, 255 (1931).

[52] Rakuzin: J. Exptl. Biol. Med., **3**, 55 (1926).

[53] Ecker and Weed: J. Immunol., **22**, 61 (1932).

[54] Ind. Eng. Chem., **1**, 665 (1909).

[55] Compt. rend., **102**, 1243 (1886).

perature, and Parravano and Mazzetti[56] placed it at 800°, at the same time calling attention to the effect of impurities on the transformation temperatures; thus, ferric oxide hastened it. Mellor[57] pointed out the absence of a definite transformation temperature and showed the change to proceed more quickly the higher the temperature of calcination. Mellor attributed the change to a conversion from amorphous to crystalline periclase, but this cannot be the case as Hedvall[58] found the oxide formed at various temperatures to have a cubic-lattice crystal structure which underwent no change on heating. The specific gravity of calcined magnesia varies, however, between 3.0 and 3.6, depending not only on the method of preparation but on the temperature of calcination. The low-temperature, low-specific-gravity oxide not only reacts much more rapidly with water than the oxide formed at high temperatures, but the former possesses a greater adsorption capacity for gases and moisture and dissolves more rapidly in acids.[59] Although the melting point of magnesia is in the neighborhood of 2500°, it undoubtedly sinters at a much lower temperature, and this change in physical character probably accounts for the difference in reactivity of the oxide ignited at different temperatures.

Magnesia Cement. It is an interesting fact that magnesia prepared by heating the chloride or nitrate to redness possesses hydraulic properties similar to Portland cement in that it sets to a rigid mass when mixed with a limited quantity of water.[60] If the nitrate is calcined at as low a temperature as 350°, the resulting magnesia will not set; if calcined at 440 to 500°, the magnesia hardens under water and at the end of 2 months is like polished marble; but if heated to 1200° or more, the oxide loses its power to set. The oxide obtained by gentle ignition of natural magnesite also possesses hydraulic properties, but that obtained from synthetic carbonates will not set, although it appears to react readily with water. This difference cannot be due to the presence of impurities in the natural product, since an hydraulic oxide is formed by converting the synthetic carbonate to nitrate and igniting the latter. The temperature of ignition and the structure of the calcined substance determine the

[56] Atti accad. Lincei (5) **30** I, 63 (1921).

[57] Trans. Ceram. Soc., **16**, 85 (1917).

[58] Z. anorg. Chem., **120**, 327 (1922).

[59] Ditte: Compt. rend., **73**, 111, 191, 270 (1871); Anderson: J. Chem. Soc., **87**, 257 (1905).

[60] Deville: Compt. rend., **61**, 975 (1865); Schwarz: Dinglers polytech. J., **186**, **25** (1867); Knapp: **202**, 513 (1872).

physical character of the oxide, and these, in turn, determine the rate of hydration and the nature of the resulting product.

Magnesia possessing setting properties is sometimes used in conjunction with lime for mortar making, in districts where only magnesium limestone is available. Similarly, gently calcined magnesia is mixed with crushed, dead-burnt magnesia in manufacturing fire-bricks so widely used in the basic Bessemer steel process. The hydraulic magnesia gives plasticity to the paste formed by mixing the materials with water to permit of molding.

Sorel's magnesia cement consists of a mixture[61] of magnesia with a concentrated solution of magnesium chloride, sp. gr. 1.16 to 1.26. This sets in a short time to a compact mass made up of minute inter-lacing crystals of the basic chloride $3MgO \cdot MgCl_2 \cdot 11H_2O$.[62] The hardened cement gives the x-ray diffraction pattern of this basic salt, and of $Mg(OH)_2$, as well as some new lines.[63] The cement possesses marked mechanical strength; it is used for cementing glass and metal and for preparing artificial stones such as *xylolith* which is made from sawdust, cement, and water.

The tendency of calcined magnesia to take up water and expand is of importance in the Portland cement industry, since the presence of as much as 2–3% of uncombined magnesia gives a concrete that will disintegrate from excessive expansion.[64]

HYDROUS ZINC HYDROXIDE

GELATINOUS ZINC HYDROXIDE

The voluminous precipitate obtained by adding the calculated amount of ammonia or alkali to a cold solution of zinc salt is hydrous zinc hydroxide, which is amorphous or consists of such extremely minute crystals that the x-ray diffraction pattern contains but two broad bands.[65] Although the hydroxide freshly formed in the cold is a transparent gel, it quickly loses water in contact with the mother liquor, becomes flocculent and later powdery, the change being accom-panied by a gradual transformation into the crystalline state.[66]

[61] Sorel: Compt. rend., **65**, 102 (1867).

[62] Maeda and Yamane: Sci. Papers Inst. Phys. Chem. Research (Tokyo) **4**, 85 (1926); *cf*. Feitknecht: Helv. Chim. Acta, **9**, 1018 (1926).

[63] Bury and Davies: J. Chem. Soc., 2008 (1932).

[64] Campbell and White: J. Am. Chem. Soc., **28**, 1273 (1906); Campbell: Ind. Eng. Chem., **1**, 665 (1909).

[65] Feitknecht: Helv. Chim. Acta, **13**, 314 (1930); Z. Krist., **84**, 173 (1933).

[66] Goudriaan: Rec. trav. chim., **39**, 505 (1920).

X-ray analysis shows that the product is zinc oxide. If the gel thrown down by mixing equivalent amounts of sodium hydroxide and zinc nitrate is washed free from the mother liquor as rapidly as possible, and dried in a vacuum desiccator over phosphorus pentoxide, the resulting product is an apparently amorphous hydroxide and not the oxide.[67] If zinc chloride or bromide is used in place of the nitrate, the amorphous hydroxide changes in part to a crystalline form of the hydroxide. The transformation to oxide is quite rapid if the precipitation is carried out at 100°.

In addition to the precipitation method above described, the highly hydrous gel is thrown down by electrolysis of alkali with a zinc anode[68] and by neutralization of concentrated alkali zincate solution.[65] The hydrous precipitates adsorb chloride, nitrate, and especially sulfate[69] so strongly that they cannot be purified completely by washing.[70]

A zinc hydroxide jelly is formed temporarily by adding 3–5 cc of N NH$_4$OH to 10 cc of 1.3 N ZnCl$_2$; but after a few minutes, it breaks spontaneously, giving a much less hydrous precipitate.[71] An organo jelly results on mixing 5% Zn(C$_2$H$_3$O$_2$)$_2$ in alcohol with an equal amount of N KOH in alcohol.[72]

CRYSTALLINE ZINC HYDROXIDES

Stable Orthorhombic Zinc Hydroxide. Large crystals of Zn(OH)$_2$, exhibiting very slight adsorption capacity, precipitate spontaneously from the alkali solution prepared in a suitable way. Thus Goudriaan[66] obtained long prismatic needles from a solution of N ZnSO$_4$ to which N KOH was added until the precipitate formed just failed to redissolve, and Fricke and Ahrendts[73] obtained small double pyramids by strong dilution of the hydroxide in strong alkali. Feitknecht[65] showed that the stable crystalline form of the hydroxide separates out in well-shaped, irregular, double pyramids from supersaturated zincate solutions having an alkali concentration up to normal. Large

[67] Feitknecht: Helv. Chim. Acta, **13**, 314 (1930); cf., also, Fricke and Ahrendts: Z. anorg. Chem., **134**, 344 (1924).

[68] Lorenz: Z. anorg. Chem., **12**, 438 (1896); Kohlschütter and Tüscher: **111**, 193 (1922); Kohlschütter and Sedelinovich: Z. Elektrochem., **29**, 30 (1923).

[69] Kurilov: Chem. Zentr., II, 1222 (1901).

[70] Goudriaan: Rec. trav. chim., **39**, 505 (1920); Fricke and Ahrendts: Z. anorg. Chem., **134**, 344 (1924); Lorenz: **12**, 439 (1896); Hall: Am. Chem. J., **19**, 901 (1897).

[71] Kurilov: Z. Elektrochem., **12**, 213 (1906).

[72] Daus and Tower: J. Phys. Chem., **33**, 605 (1929).

[73] Z. anorg. Chem., **134**, 344 (1924).

crystals are also obtained by dissolving the freshly formed, thoroughly
washed gel in ammonia and removing the ammonia gradually by
placing the solution and concentrated sulfuric acid in separate beakers
under a bell jar.[74]

X-ray analyses of the crystals ordinarily obtained from alkali
zincate solutions have been made by several people,[75] who agree
that the crystals belong to the orthorhombic system.   In this respect
zinc hydroxide differs from the hydroxides of the other divalent metals
which crystallize in the hexagonal system.   The x-ray diffraction
pattern is shown diagrammatically in Fig. 32a after Feitknecht.
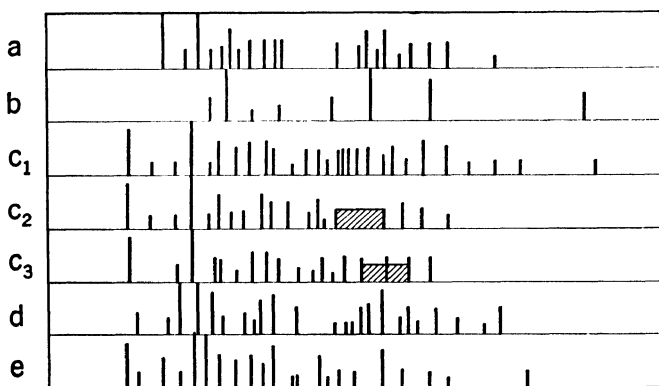
FIG. 32.—Diagrams of the x-ray diffraction patterns of (a) rhombic $Zn(OH)_2$;
(b) α-$Zn(OH)_2$; ($c_1c_2c_3$) β-$Zn(OH)_2$; (d) γ-$Zn(OH)_2$; (e) δ-$Zn(OH)_2$.

α-Zinc Hydroxide.   An x-ray diffraction pattern entirely different
from that for the orthorhombic hydroxide was obtained by Fricke[37]
from a freshly prepared hydrous precipitate thrown down from a solu-
tion of zinc chloride with a slight excess of sodium hydroxide.   This
was confirmed and extended by Feitknecht,[65] who obtained the same
pattern for the hydroxide resulting from the lixiviation of basic zinc
salts such as the basic zinc halides (Fig. 32b).   It was suggested that
the formation of this hydroxide by direct precipitation may take place
through the intermediate formation of a basic salt, but it is not obvious
why this should be necessary.   An x-ray analysis of the crystals[76]
disclosed that they belonged to the hexagonal system like the hydrox-

[74] Dietrich and Johnston: J. Am. Chem. Soc., **49**, 1419 (1927).

[75] Natta: Atti accad. Lincei (6) **2**, 495 (1926); Gottfried and Mark: Z. Krist., **65**,
416 (1927); Corey and Wyckoff: **86**, 8 (1933).

[76] Feitknecht: Z. Krist., **84**, 173 (1933).

ides of the other divalent metals. This so-called α-hydroxide is never formed as well-defined crystals but always in a highly dispersed, gelatinous or pseudomorphous form.

β-, γ-, and δ-Zinc Hydroxides. In addition to the orthorhombic and hexagonal forms of the hydroxide, Feitknecht obtained three other metastable forms which give distinctly different x-ray diffraction patterns and which go over to the stable orthorhombic hydroxide in contact with dilute alkali. The so-called β-hydroxide separates as variously shaped somatoids from supersaturated zincate solutions in very dilute alkali (less than 0.05 N). The x-ray patterns for preparations obtained in three slightly different ways are shown in Fig. 32 ($c_1 c_2 c_3$). The γ-hydroxide is obtained in the form of long needles by the action of 0.1 to 0.4 N alkali solution on the α-hydroxide; and a number of other shapes of crystals and aggregates result by crystallization of strongly supersaturated zincate solutions containing 0.1–0.8 N alkali. These crystals give the diffraction pattern shown in Fig. 33d. The δ-hydroxide is formed by the slow hydrolysis of zincate solutions containing 0.35–0.75 N alkali. The crystals give the pattern shown in Fig. 33e.

Since it is unusual to have so many allotropic modifications of a compound, one may be inclined to doubt the conclusions of Feitknecht and to interpret the different x-ray patterns for the so-called β-, γ-, and δ-hydroxides to the existence of solid solutions of the hexagonal and orthorhombic forms rather than to the formation of definite individuals. Feitknecht doubtless considered this as a possible interpretation and discarded it as improbable. He considers the polymorphism to result from the strong polarizing action of zinc ion on the hydroxyl ion. This polarizing action exerts itself also in imparting to zinc hydroxide an amphoteric character which is much more pronounced than in the other divalent hydroxides.

ZINC HYDROXIDE SOL

If a zinc hydroxide gel is washed by the aid of the centrifuge, peptization results to a certain extent, giving a dilute sol[72] which coagulates spontaneously within a day or two owing to the growth of relatively large crystalline aggregates. A sol consisting of both zinc oxide and hydroxide is formed by dipping red-hot zinc into water,[77] and by allowing zinc to stand for a long time in contact with air.[78]

[77] Kimura: Mem. Coll. Sci. Eng., Kyoto Imp. Univ., **5**, 211 (1913).

[78] Traube-Mengarini and Scala: Kolloid-Z., **10**, 115 (1912); Nordenson: Kolloid-Beihefte, **7**, 106 (1915).

With the exception of alkali-peptized colloids to which reference will be made in the next section, concentrated sols of zinc hydroxide have been obtained only in the presence of protecting colloids such as potassium soaps[79] and sodium protalbinate.[80]

Solutions in Alkali

The newly formed gel of zinc hydroxide dissolves readily in alkali, 1 atom of Zn^{++} being taken up by approximately 6 of OH^-.[81]   On account of the aging and accompanying crystallization of the hydroxide, the solubility in alkali as well as in ammonia is less the older and less hydrous the preparation.[82]

Because of the weak acidic character of zinc hydroxide, Hantzsch[83] believed that alkalis peptize the gel, forming a sol from which most of the hydroxide precipitates on standing, leaving the remainder in solution as zincate.   Since Hantzsch worked with dilute alkali solutions he was probably right in concluding that most of the gel was peptized, at least at the outset.   There is no doubt, however, that solutions in concentrated alkali contain zincate.   The more concentrated the alkali the more hydroxide it will take up and the more zincate will form.[84]   Goudriaan[66] determined the 30° isotherm for the system, Na_2O-ZnO-H_2O.   The saturation concentration increases rapidly to the triple point, ZnO-$Na_2ZnO_2 \cdot 4H_2O$, where the composition of the solution in weight per cent is 27.8% Na_2O and 16.5% ZnO.   The zincate forms well-developed crystals decomposed by water and is stable from the triple point to the quadruple point, $Na_2ZnO_2 \cdot$-$4H_2O$-$Na_2O \cdot 3H_2O$-H_2O, at 39.2% Na_2O and 9.7% ZnO.   Sodium zincate forms an incongruent solution, the addition of water to the solid salt or the dilution of the solution causing ZnO to precipitate. This accounts for a number of so-called sodium zincates[85] which are either metastable or non-existent.

In opposition to Goudriaan, Fricke and Ahrendts[73] and Müller[86] claim to get crystals of the acid zincate, $NaHZnO_2$, rather than the

[79] Kurilov: Z. Elektrochem., **12**, 213 (1906); Roth: German Pat. 228,139 (1908).

[80] Paal and Hartmann: Ber., **51**, 894 (1918); Amberger: German Pat. 229,306 (1909).

[81] Rubenbauer: Z. anorg. Chem., **30**, 331 (1902); Herz: **28**, 474 (1901).

[82] Hantzsch: Z. anorg. Chem., **30**, 289 (1902); Kunschert: **41**, 337 (1904).

[83] Hantzsch: Z. anorg. Chem., **30**, 300 (1902).

[84] Klein: Z. anorg. Chem., **74**, 157 (1912); Rubenbauer: **30**, 331 (1902); Wood: J. Chem. Soc., **97**, 878 (1910).

[85] *E.g.*, Comey and Jackson: Am. Chem. J., **11**, 145 (1889).

[86] Z. Elektrochem., **33**, 134 (1927).

normal salt from strongly alkaline solutions (14–19 N). From electromotive determinations on adding sodium hydroxide to solutions of zinc salts Hildebrand and Bowers[87] obtained evidence of the formation of acid zincate even in relatively dilute alkali. This could not be confirmed by Britton,[33] who reached the very probable conclusion that a part of the hydroxyl ion is removed by adsorption on zinc hydroxide, giving a negative sol,[88] and a part reacts to give zincate. The presence of sugar facilitates the peptization of the hydroxide by alkalis.[89]

Zinc hydroxide dissolves in ammonium hydroxide with the formation of $Zn(NH_3)_4(OH)_2$.

Zinc oxide in the finely divided or colloidal state finds its most important application in the anhydrous rather than the hydrous condition. Thus, when zinc white alone, or mixed with finely ground silica or calcium carbonate is ground with linseed oil, it forms a white paint that does not discolor in the presence of hydrogen sulfide. A suitable mixture of zinc white and of finely divided zinc hydroxide precipitated in the cold is said to form a useful enamel pigment.[90] Zinc oxide has a mild antiseptic action, and a sol consisting of the oxide, gutta percha, and Venice turpentine is applied to cloth in the manufacture of surgeons' adhesive tape. Like magnesia, a wet mixture of zinc oxide and chloride sets to a solid gel. A strong dental cement consists of a mixture of zinc oxide and aluminum phosphate. The oxide also finds some applications in face powders, in glazes, and as a filler in oilcloth and celluloid; but by far the greatest demand is as a filler and pigment in rubber goods, especially automobile tires. In recent years it has been used to advantage as a hydrogenation catalyst in such processes as the catalytic synthesis of methyl alcohol from carbon monoxide and hydrogen.

HYDROUS CADMIUM HYDROXIDE

Hydrous cadmium hydroxide precipitates in a voluminous form when fairly concentrated solutions of cadmium salts are treated with alkali or ammonia. Even when the precipitates are thrown down at 0°, they give an x-ray diffraction pattern[91] showing that they are made up of crystals of the hydroxide which belong to the hexagonal

[87] J. Am. Chem. Soc., **38**, 785 (1916); cf., also, Kunschert: Z. anorg. Chem., **41**, 337 (1904); Foerster: Z. Elektrochem., **6**, 16 (1898).

[88] Cf. Mohanlal and Dhar: Z. anorg. Chem., **174**, 1 (1928).

[89] Mehrotra and Sen: J. Indian Chem. Soc., **4**, 117 (1927).

[90] Lance and Joannis: J. Soc. Chem. Ind., **25**, 486 (1906).

[91] Hüttig and Mytyzek: Z. anorg. Chem., **190**, 353 (1930).

system.[92]   The purest form is obtained from the nitrate, since the gel adsorbs nitrate less strongly than chloride or sulfate.[93]   Lorenz[94] claims to get the hydroxide by electrolysis of alkali chloride with a cadmium anode and a platinum cathode.   The hydroxide may be obtained in the form of a jelly by precipitation from a glycerol solution with alcoholic potassium hydroxide.

Like the corresponding zinc compound, cadmium hydroxide is soluble in excess ammonia; but unlike the former it is only slightly soluble in dilute alkalis.[95]   Hot, highly concentrated solutions of potassium hydroxide carry considerable amounts into solution from which hexagonal plates of cadmium hydroxide crystallize.[39]

Alkali sulfides react with the fresh gel formed in the cold, giving yellow cadmium sulfide, and with the aged hydroxide, giving red cadmium sulfide.   Since the yellow and red sulfides were thought to be polymers, Büchner[96] assumed the existence of two forms of cadmium hydroxide.   Although there are two allotropic modifications of cadmium sulfide, it was found in the author's laboratory by Milligan[97] that both modifications may be either yellow or red, depending on the size and nature of the surface of the particles.   Rapid action of the voluminous compound with alkali sulfides gives small yellow particles, whereas the slower action with the denser aged hydroxide gives larger particles that appear red.

The hydroxide starts to decompose on heating at a temperature that varies with the method of formation and age of the precipitate. By the aid of the dehydration isobars at 10-mm vapor pressure, Hüttig and Mytyzek showed[98] that, in most samples, rapid decomposition takes place between 150 and 175°, but certain samples decompose rapidly around 120°.   Unlike magnesia and calcium oxide, cadmium oxide does not rehydrate in the presence of water.

HYDROUS MERCURIC OXIDE

Hydrous mercuric oxide is thrown down as a yellow flocculent mass on adding alkali to a cold mercuric solution.   It does not form

[92] Natta: Atta accad. Lincei (6) **2**, 495 (1926).

[93] Bonsdorff: Z. anorg. Chem., **41**, 137 (1904).

[94] Z. anorg. Chem., **12**, 439 (1896).

[95] Piater: Z. anorg. Chem., **174**, 321 (1928).

[96] Ber., **20**, 681 (1887); *cf.* Klobukoff: J. prakt. Chem. (2) **39**, 412 (1887).

[97] J. Phys. Chem., **38**, 797 (1934); *cf.* Allen and Crenshaw: Am. J. Sci. (4) **34**, 341 (1912).

[98] Z. anorg. Chem., **190**, 353 (1930); Hackspill and Kieffer: Ann. chim. (10) **14**, 227 (1930).

the monohydrate or hydroxide $Hg(OH)_2$, as claimed by Carnelley and Walker,[99] nor does it retain its adsorbed water very strongly, but is readily dried to the anhydrous oxide.[100] If the yellow oxide is boiled with aqueous solutions of salts or the dried oxide is heated, the color changes to orange-red. This red compound is formed directly by the thermal decomposition of mercuric nitrate. As usually obtained, the yellow oxide decomposes at a lower temperature, is more soluble in water, and reacts more readily with acids, alkalis, and salts than the red compound. These distinct differences in the physical and chemical properties were attributed by Gay-Lussac,[101] and later by W. Ostwald[102] and others, to a difference in the degree of fineness of the particles, the greater activity of the yellow oxide resulting from the greater surface of the smaller particles. This view was called in question by Glazebrook and Skinner[103] and by Cohen,[104] who showed that the electromotive force of the chain: Hg | HgO (red), KOH, HgO (yellow) | Hg, was 0.685 millivolt, indicating the existence of two isomeric modifications of the oxide; but Allmand[105] traced these results to the variation in solubility of particles of different size.[106] Schoch[107] attributed the difference in properties to a difference in crystal structure, the yellow oxide consisting of quadratic plates and the red of prisms. Allmand confirmed Schoch's observation but showed conclusively that either type of crystal may be yellow or red, depending altogether on the state of subdivision of the particles. From x-ray diffraction studies, Levi[108] demonstrated that both yellow and red mercuric oxide give the same x-ray diffraction pattern. This was confirmed by Fricke[37] and by Zachariasen.[109] The latter showed further that the crystals belong to the rhombic system, the mercury atom forming a body-centered lattice.

[99] J. Chem. Soc., 53, 59 (1888); cf. Schaffner: Ann., 51, 182 (1844).

[100] Schoch: Am. Chem. J., 29, 321 (1903); cf. Millon: Ann. chim. phys. (3) 18, 333 (1846).

[101] Compt. rend., 16, 309 (1843).

[102] Z. physik. Chem., 18, 159 (1895); 34, 495 (1900); Schick: 42, 155 (1902); Varet: Compt. rend., 120, 622 (1895).

[103] Proc. Roy. Soc. (London) 51, 60 (1892).

[104] Z. physik. Chem., 34, 69 (1900).

[105] Z. Elektrochem., 16, 254 (1910).

[106] Cf. Hulett: Z. physik. Chem., 37, 385 (1901).

[107] Am. Chem. J., 29, 321 (1903).

[108] Gazz. chim. ital., 54, 709 (1924); 58, 417 (1928); cf., however, Kolkmeijer: Verstag. Akad. Wetensch. Amsterdam, 36, 1084 (1927).

[109] Z. physik. Chem., 128, 421 (1927).

A stable yellow sol is obtained by precipitating hydrous mercuric oxide in the presence of Paal's[110] sodium salts of protalbinic and lysalbinic acids, which act as protecting colloids. After dialysis, this is agglomerated by acids and certain salts, giving a gelatinous precipitate. By adding mercuric chloride to a normal solution of potassium hydroxide containing 40 cc of acetone, a sol is obtained which sets to a firm jelly on standing, the time required depending on the concentration of sol.[111] The setting may be hastened by adding a small amount of acid or by heating; but too much heating causes agglomeration to a gelatinous precipitate. For some unknown reason, the presence of even a small amount of mercurous salt seems to retard or prevent jelly formation.

Mercurous oxide does not exist. The precipitate formed by adding alkali to a mercurous salt was found by x-ray analysis to consist of a mixture of mercury and mercuric oxide.[112]

[110] Ber., **35**, 2219 (1902); *cf.* Kalle and Co.: Z. angew. Chem., **20**, 1374 (1907); May: German Pat. 248,526 (1911).

[111] Bunce: J. Phys. Chem., **18**, 269 (1914); Reynolds: Proc. Roy. Soc. (London) **19**, 431 (1871).

[112] Fricke and Ackermann: Z. anorg. Chem., **211**, 233 (1933).

CHAPTER VII

THE HYDROUS OXIDES OF SILICON AND GERMANIUM

HYDROUS SILICON DIOXIDE

Hydrous silicon dioxide is obtained as a clear transparent jelly, as a partly dried jelly named silica gel, and as a sol. The several forms will be taken up in order.

SILICA JELLY

FORMATION

Hydrogels. Hydrous silica in the form of a jelly is usually prepared by adding acid to a fairly concentrated solution of sodium metasilicate or of water glass, which is a colloidal system containing negatively charged particles of silica and soda stabilized by preferential adsorption of hydroxyl ion.[1] The jelly is also formed by hydrolysis of silicon sulfide, tetrachloride,[2] and tetrafluoride,[3] or of ethyl silicate[4] and methyl silicate.[5] It results also when a silica sol is rendered too pure by dialysis and coagulates spontaneously. The jelly formed by any of the above methods may be broken up by stirring and washing to remove most of the soluble impurities.

The time required for a mixture of silicate and acid to set to a firm coherent jelly has been the subject of extended investigations especially by Flemming,[6] Holmes,[7] Prasad,[8] and Hurd.[9] In general,

[1] Stericker: Chem. & Met. Eng., 25, 61 (1921).

[2] Langlois: Ann. chim. phys. (3) 52, 331 (1858); Schwarz and Richter: Ber., 62B, 31 (1929).

[3] Berzelius: Ann. chim. phys. (2) 14, 366 (1820).

[4] Ebelmen: Ann. chim. phys. (3) 16, 129 (1846); Dearing and Reid: J. Am. Chem. Soc., 50, 3058 (1928); Thiessen and Koerner: Z. anorg. Chem., 189, 168, 174 (1930); Inaba: Sci. Papers Inst. Phys. Chem. Research (Tokyo) 15, 278 (1930).

[5] Grimaux: Compt. rend., 98, 1437 (1884).

[6] Z. physik. Chem., 41, 427 (1902).

[7] J. Phys. Chem., 22, 510 (1918).

[8] Prasad and Hattiangadi: J. Indian Chem. Soc., 6, 653, 893, 991 (1929); 7, 341 (1930); Prasad: (Ray Commemorative Volume) 119 (1933).

[9] Hurd and Letteron: J. Phys. Chem., 36, 604; Hurd and Miller: 2194 (1932); Hurd and Carver: 37, 321 (1933); Hurd and Swanker: J. Am. Chem. Soc., 55, 2607 (1933); Hurd, Raymond, and Miller: J. Phys. Chem., 38, 663 (1934).

the time of set of the mixture without foreign addition agents depends on the concentration of silica, the pH value, and the temperature.[6] Neutral or slightly acid mixtures set the most rapidly.[8] With increasing concentration of acid the rate of set falls off and then increases rapidly once more,[7] possibly owing to the dehydrating action of the large excess of acid. Between $pH = 4.2$–5.5 for hydrochloric acid and between $pH = 4.4$–6.0 for acetic acid, the rate of set is a linear function of the hydrogen ion concentration.[9] The effect of temperature on the time of set appears to be the same, regardless of the soda:silicate ratio in the water-glass solution.[9] Considering the process according to the laws for the velocity of ordinary chemical reactions, Hurd[9] obtained a value of 16,640 calories, which is analogous to Arrhenius' heat of activation for homogeneous chemical change. The initial state of the process consists of the chemical change which gives a sol, negative in alkaline solution and positive in acid solution. During the sol formation, the surface tension of the mixture[9] undergoes but little change; the sol coagulates spontaneously under the influences of the electrolytes present, without any appreciable heat effect but with a rapid rise in the surface tension. The addition of electrolytes, especially those with multivalent coagulating ions, increases the rate of set. On the other hand, sodium sulfate, chloride, and nitrate appear to decrease the time of set appreciably without causing any considerable change in the pH value. Non-electrolytes or weak electrolytes which do not influence the pH value have comparatively little effect on the rate of set.[9] No appreciable change in the electrical conductivity takes place during the setting process, indicating that the gel possesses a sponge rather than a honeycomb structure.

Organogels. In the first chapter, mention was made of the fact that the water in silica gel can be replaced by organic liquids such as alcohol, acetone, benzene, chloroform, etc. Graham[10] claimed to remove practically all the water by repeated immersion of the hydrogel in absolute alcohol. Neuhausen and Patrick[11] were unable to reproduce Graham's results and pointed out the great difficulty in replacing all the water adsorbed on the gel. Furth and Purse[12] showed, however, that a gel containing but 0.57% water associated with 30.3% alcohol could be obtained by passing dry air saturated

[10] J. Chem. Soc., **17**, 368 (1864).
[11] J. Am. Chem. Soc., **43**, 1844 (1921); *cf.* Berl and Burkhardt: Z. anorg. Chem., **171**, 102 (1928).
[12] J. Phys. Chem., **30**, 617 (1926).

with alcohol vapor over the hydrogel; and Rao and Doss[13] reduced the water content to 0.21%, associated with 7% alcohol, by extracting the gel with absolute alcohol in a Soxhlet extractor. It thus appears that almost, if not quite, pure organogels can be made by displacement of water from the hydrogel.

COMPOSITION

Silica gel thrown down from aqueous solution is frequently referred to as the hydrogel of silicic acid, the connotation being that the solid framework of the gel is one or more of the silicic acids rather than silica. In answering the question of the composition of the gel van Bemmelen[14] climaxed his classic investigations on the hydrous oxides by his exhaustive study of the dehydration and the rehydration of the precipitate thrown down from alkali silicate solution with dilute hydrochloric acid. A silica jelly containing 300 mols of water to 1 of silica is very soft, and when broken into pieces, it flows together like a viscous liquid. A gel with a water content of 30 to 40 mols is brittle; and with 6 mols, it can be pulverized, giving an apparently dry powder. On further dehydration, the vapor-pressure curve drops continuously, giving no indication of a definite hydrate. The highly hydrous oxide is almost perfectly clear, but when the water content drops to a point usually between 1.5 and 3.0 mols, depending on the method of preparation and the history of the sample, the gel becomes opaque and chalky but clears up once more when the water content is reduced to 0.5–1.0 mol. The clouding is due to the appearance of air bubbles in the pores of the gel and lasts until the pores are completely filled with air. Owing to capillary action, the water which evaporates from the outer surface of the capillaries is replaced from the inside of the gel, leaving a vapor space in the center of the jelly and thus producing an opacity which lasts until the pores are free from capillary water. The remaining 0.5 to 1.0 mol is adsorbed very strongly on the surface of the particles and can be removed only by heating to a relatively high temperature.

The vapor-pressure isotherm at 15° for hydrous silica, as obtained by Anderson,[15] is given in Fig. 33, which is similar in all essential respects to that obtained by van Bemmelen. The direction of the arrows shows whether water is being taken up or given off. Starting with a fresh jelly, the vapor pressure falls below that of pure water

[13] J. Phys. Chem., **35**, 3486 (1931).
[14] "Die Absorption," 196, 214, 232 (1910).
[15] Z. physik. Chem., **88**, 191 (1914).

and decreases along the curve AO, the volume decreasing simultaneously.   No actual break occurs at O, where the gel begins to cloud.
The volume does not change much after reaching O, and the loss of
water along the curve OO_1 causes the pores to fill up with air, the gel
becoming cloudy.   At O_1, the pores are filled with air except for a
sma ll amount of strongly adsorbed water, and the gel is clear again.
Alo ng O_1B most of the adsorbed water is lost.   The 15° isotherm does
not end at the origin since a higher temperature is required to remove
the last trace of adsorbed water.   If the dehydration is stopped at
some point D along the curve AO and the gel is subsequently subjected
to a higher partial pressure of water vapor, the hydration is not reversi-
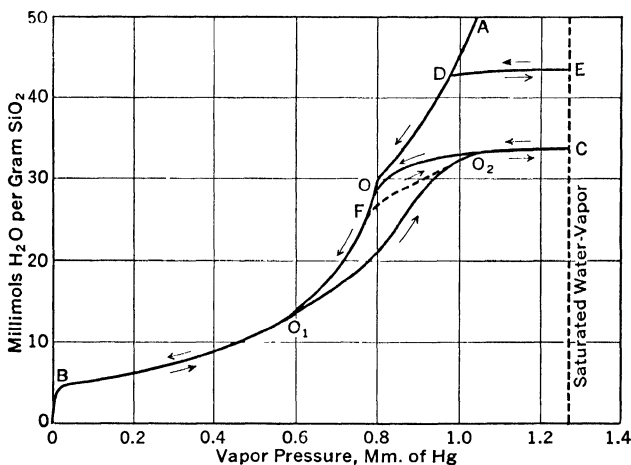
FIG. 33.—Vapor-pressure isotherm of hydrous silica at 15°.

ble, but a curve, DE, is obtained.   This is because the gel shrinks
along AO, and as it does not swell to any marked extent, the water is
not taken up under the same conditions.   If dehydration is stopped
at any point F along OO_1, hydration curves like that indicated by the
dotted line are obtained.   From O_2 to C and from O_2 to O, the pres-
sure-concentration curves are reversible.   It is possible to pass along
the path OO_1O_2O as often as one pleases, but only in the one direction
indicated.   The existence of this hysteresis loop was confirmed by
Anderson with the systems gel-water, gel-alcohol, and gel-benzene.
Both van Bemmelen and Anderson [15] explained the hysteresis from the
known fact that a liquid in a capillary tube has a greater vapor pres-
sure when being filled than when being emptied, as in the former there
is a diminution of the curvature of the liquid meniscus, due to incom-

plete wetting. Zsigmondy[16] attributed the marked hysteresis to adsorbed air which prevents the silica surface from being wetted readily. As a matter of fact, Patrick and McGavack[17] found no hysteresis in the adsorption of sulfur dioxide by silica gel when special precautions were taken to remove all air from the system. Moreover, no hysteresis was observed in the adsorption of sulfur dioxide, alcohol, carbon tetrachloride, and benzene by a dynamic method which consists in passing a mixture of air and the vapor in question over the adsorbent until equilibrium is attained.[18] The experimental difficulties are greater with water,[18] but in this case also Patrick[19] demon-
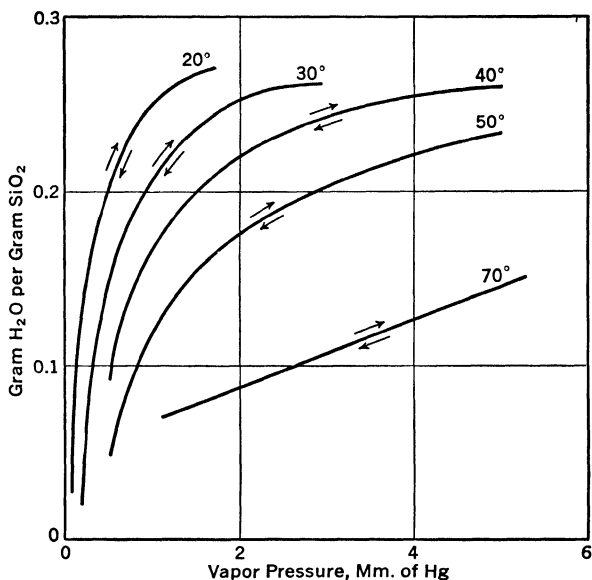
FIG. 34.—Vapor-pressure isotherms of hydrous silica in the absence of air. (No hysteresis.)

strated the absence of any hysteresis in the adsorption and desorption of water vapor when the necessary precautions were taken to exclude all air. Curves which represent both the adsorption and desorption at various temperatures are reproduced in Fig. 34. These curves are

[16] "Kolloidchemie," 161 (1912).

[17] J. Am. Chem. Soc., **42**, 946 (1920).

[18] Patrick and Opdycke: J. Phys. Chem., **29**, 601 (1925); cf. Lambert and Clark: Proc. Roy. Soc. (London) **122A**, 497 (1929); Lambert and Foster: **134A**, 246 (1931); **136A**, 363 (1932).

[19] Colloid Symposium Annual, **7**, 129 (1930); cf., however, Pidgeon: Can. J. Research, **10**, 713 (1934).

significant not only in showing the absence of the hysteresis phenomenon but, more important, in failing to show the presence of any flex at any point in the several curves.   In all previous work, a relatively small adsorption was observed at low pressures which increased greatly after a certain supposedly definite pressure of water vapor was reached. This region of large adsorption at relatively constant pressure O_1O of Fig. 33 was supposed by Zsigmondy to mark the beginning of capillary adsorption.   Hückel[20] likewise distinguished capillary condensation from surface adsorption on the basis of evidence supplied by a study of the silica-water system.   Patrick points out that this conclusion is based on erroneous experimental results.   The discontinuities observed in the earlier work were due entirely to the presence in the gel of permanent gases which interfered with the wetting during the adsorption measurements and so produced pseudo equilibria.

Since the point O in Fig. 33 may represent approximately 2 mols of water to 1 of silica and the point O_1 approximately 1 mol of water to 1 of silica, one may be inclined to regard the dehydration process as the decomposition of definite hydrates.   Van Bemmelen showed this point of view to be untenable since the points O and O_1 do not correspond, in the vast majority of cases, with 2 mols and 1 mol of water, respectively, but vary with the history of the sample between 1.5 and 3 with the former and 0.5 and 1 with the latter.   Moreover, one gets the same form of curves and optical phenomena by substituting for water such liquids as alcohol, benzene, and carbon tetrachloride.   Van Bemmelen's work has been confirmed and extended and his conclusions reaffirmed by a number of investigators, among whom may be mentioned Löwenstein,[21] Zsigmondy,[22] Thiele,[23] Anderson,[15] Bachmann,[24] Vanzetti,[25] Lenher,[26] and Berl and Urban.[27]   Tschermak,[28] on the other hand, champions the view that the action of hydrochloric acid on mineral silicates yields definite silicic acids corresponding to the salts from which they are obtained.   Tschermak's conclusions from

[20] "Adsorption und Kapillarkondensation" (1928).

[21] Z. anorg. Chem., **63**, 69 (1909).

[22] Zsigmondy, Bachmann, and Stevenson: Z. anorg. Chem., **75**, 189 (1912).

[23] Dissertation, Leipzig (1913).

[24] Z. anorg. Chem., **100**, 77 (1917),

[25] Gazz. chim. ital., **47** I, 167 (1917).

[26] J. Am. Chem. Soc., **43**, 391 (1921).

[27] Z. angew. Chem., **36**, 57 (1923).

[28] Z. physik. Chem., **53**, 351 (1905); Centr. Mineral., Geol., 225 (1908); Z. anorg. Chem., **63**, 230 (1909); **87**, 300 (1914); Norton and Roth: J. Am. Chem. Soc., **19**, 832 (1897); cf. Hillebrand: Sitzber. Akad. Wiss. Wien. **115**, 697 (1906).

dehydration experiments were shown to be altogether unwarranted, by Jordis,[29] van Bemmelen,[30] Mügge,[31] Serra,[32] and Thiele,[23] since the breaks in the composition curves are determined by the temperature at which the drying takes place, the nature of the drying agent, and the age and history of the sample. In spite of the evidence piled up against the existence of definite silicic acids in the solid state, people are still attempting to establish their identity. Thus Schwarz and Menner[33] claim to remove adsorbed water by Willstätter's method of washing the gelatinous oxide with alcohol and acetone. By a suitable choice of the conditions of preparation and dehydration, the existence of H_2SiO_3, $H_2Si_2O_5$, $H_2Si_3O_7$, and $H_4Si_3O_8$ is regarded as definitely established; and the individuality of $12SiO_2 \cdot 10H_2O$ and $12SiO_2 \cdot 9H_2O$ is believed probable. In addition to these, Thiessen and Koerner[34] claim to get acids in which the silica to water ratio is 2 : 5, 1 : 2, and 2 : 3 by hydrolysis of ethyl silicate. Thus, at least nine definite silicic acids are assumed to exist in the solid state.[35] As a matter of fact, these observations merely confirm what everybody knows, that one can get a composition for a gelatinous body corresponding to almost any desired formula provided one chooses the conditions properly. After considerable experience in the dehydration of hydrous materials, the author is inclined to believe that many of the breaks and points of inflection which are attributed to hydrates in the curves obtained by Thiessen, Simon, and others, are the results of failure to attain an equilibrium state.

Finally, the most conclusive evidence against the view that hydrous silica consists of one or more silicic acids is furnished by the x-ray studies of Krejci and Ott,[36] who showed that a freshly prepared sample, which had at no time been heated above 100°, gave an x-ray diffraction pattern of the cristobalite type. It thus appears that crystalline centers of colloidal dimensions are found in freshly prepared

[29] Z. angew. Chem., **19**, 1697 (1906).

[30] Z. anorg. Chem., **59**, 225 (1908).

[31] Centr. Mineral., Geol., 129, 326 (1908).

[32] Atti accad. Lincei (5) 19 I, 202 (1910).

[33] Ber., **57B**, 1477 (1924); **58B**, 73 (1925); Schwarz: Z. Elektrochem., **32**, 415 (1926); Schwarz and Richter: Ber., **62B**, 31 (1929).

[34] Z. anorg. Chem., **189**, 168, 174 (1930); **197**, 307 (1931).

[35] *Cf., also,* Willstätter and Kraut: Ber., **59B**, 2541 (1926); **64B**, 1709 (1931): Willstätter, Kraut, and Lobinger: **61B**, 2280 (1928); **62B**, 2027 (1929); Biltz and Rahlfs: Z. anorg. Chem., **172**, 273 (1928); Simon and Rath: **202**, 191 (1931); Treadwell and Wieland: Helv. Chim. Acta, **13**, 842 (1930).

[36] J. Phys. Chem., **35**, 2061 (1931).

hydrous silica at ordinary temperatures and that the crystals are the cristobalite modification of silica rather than a silicic acid.   Schwarz and Richter give a photograph of an x-radiogram which they claim is the diffraction pattern for $H_2Si_2O_5$.   They give no description as to how the pattern was obtained; hence there is no way of telling whether it is really the pattern of a true acid, of some impurity in the gel, or, most likely, of cristobalite.   Pascal[37] analyzed three types of hydrous silicon dioxide magnetically and found all of them to behave like mixtures of the anhydrous oxide and water.[38]

<div align="center">PROPERTIES</div>

This section will be concerned with certain characteristics of silica jelly other than adsorption which will be considered in a separate section.

Chemical Properties

Silica jelly consists of extremely minute particles of silica joined together into an enmeshing network which holds water both by adsorption on the surface of the particles and in minute pores which appear to be of the order of magnitude of 5 mμ or less in diameter.[15]   As already indicated, the freshly formed oxide consists of crystalline centers of cristobalite.   These are prevented from growing because the initial formation of crystals increases the viscosity to such an extent that the free movement of the atoms and molecules is prevented.   The dried gel can be heated to temperatures below 1000° without imparting sufficient mobility to the atoms and molecules to continue the interrupted growth of the crystals; but a sample of gel heated to 1150° for 5 hours gives a very clear x-ray pattern for cristobalite,[36] indicating that this temperature is sufficient to bring about an increase in crystal size.

The properties of hydrous silica show the usual variations in both physical and chemical properties with the temperature of precipitation.   The gel formed by hydrolysis of silicon fluoride at 0° is much more readily soluble in hydrofluoric acid and sodium hydroxide and has a much stronger adsorptive capacity for methylene blue than the oxide formed at 100°.   Schwarz and Liede[39] considered the two oxides to be distinct modifications of silica, but there is no experimental justification for this assumption.   The difference is due to variations in

[37] Compt. rend., **175**, 814 (1922).
[38] *Cf.* Le Chatelier: Compt. rend., **147**, 660 (1908).
[39] Ber., **53B**, 1509, 1680 (1920).

specific surface resulting from agglomeration of primary particles into denser aggregates. Indeed, Schwarz and Liede studied the gradual spontaneous loss of water and agglomeration of oxide particles and found the processes to be continuous. At first they regarded the aging as a definite chemical condensation from $(SiO_2)_x$ to $(SiO_2)_{2x}$, but later they considered it to consist in the spontaneous loss of water from orthosilicic acid with the formation of a continuous series of condensed silicic acids in which the $SiO_2 : H_2O$ ratio becomes greater and greater. Until there is some definite proof of the alleged polymerization or of the formation of polysilicic acids, it seems preferable to regard the aging as a process of agglomeration and the decrease in reactivity and in water content as a necessary result of decreasing density and specific surface.

Elasticity

Although silica is classified as a non-elastic body, the freshly formed jelly possesses an elasticity of the same order of magnitude as that of a gelatin jelly.[40] As in a gelatin jelly, the elasticity modulus varies greatly with the water content of the sample and increases markedly on aging.[41]

The elastic-plastic properties of acid, neutral, and alkaline silica jellies have been studied in some detail by Kröger and Fischer.[42] For samples of the same age, the elastic properties of the various jellies are not very different. The plastic properties increase on passing from acid to alkaline jellies. For the same jelly, the plastic properties fall off with decreasing temperature and also with aging.

Silica jellies possess the interesting property of vibrating like a rigid body under certain conditions.[43] Holmes, Kaufmann, and Nicholas[44] obtained jellies in a glass tube that gave a tone two octaves above middle C when the vessel was struck. If the jellies were prevented from touching the glass tube by coating the walls with vaseline, the vibration frequency was much lower than for similar jellies adhering to the walls. The vibration frequency is increased by decreasing the concentration of silica and by the presence of excess mineral acid, factors which increase the tension and thus the effective rigidity. The same factors increase the tendency of the jelly to

[40] Prasad: Kolloid-Z., **33**, 279 (1923).
[41] Hatschek: J. Phys. Chem., **36**, 2994 (1932).
[42] Kolloid-Z., **47**, 5, 10, 14 (1929).
[43] Kohlrausch: Z. physik. Chem., **12**, 773 (1893).
[44] J. Am. Chem. Soc., **41**, 1329 (1919).

synerize, thus showing that both vibration and syneresis have a direct relation to tension.   Holmes believed the vibration to be transverse, the vibration frequency varying approximately inversely as the diameter of the cylinder of jelly.   Prasad[40] failed to confirm these conclusions for gels removed from the vessels in which they were made.   The tone emitted by a given jelly showed wide variation depending on how it was held.   Moreover, by applying Newton's formula for the velocity of propagation of a longitudinal wave, the vibrations were shown to be longitudinal rather than transverse.

In this connection it may be mentioned that Kröger and Fischer[42] prepared lenses of silica jelly which were sufficiently perfect optically that photographs could be taken by means of them.

Syneresis

Silica jelly furnishes a noteworthy example of the property of jellies in general to contract and exude liquid without breaking.   This

	Concentration g SiO_2/100 Cc.	Setting Time hrs.	Induction Period hrs.
I	798	0.012	0.030
II	532	0.045	0.075
III	399	10.0	20.0
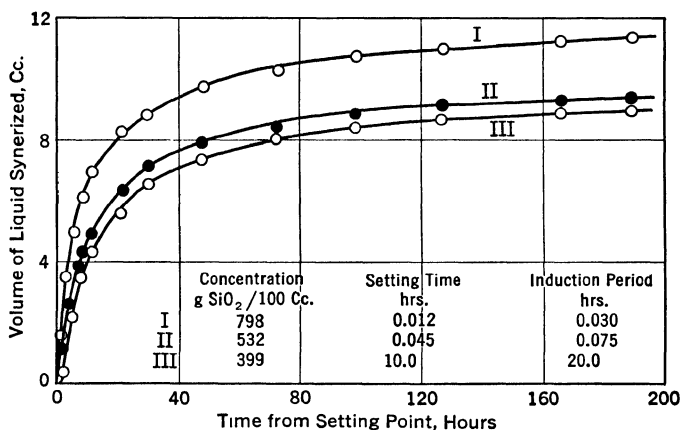
FIG. 35.—Effect of silica concentration of gel on the velocity of syneresis.

phenomenon, known as syneresis, was first observed by Graham[45] in silica jellies.   The phenomenon with these jellies has been studied by Holmes[44] and especially by Ferguson and Applebey.[46]   In Fig. 35 are reproduced some curves of the latter which show the rate of syneresis as measured by the volume of liquid exuded from jellies prepared by adding water-glass solution to acetic acid.   Additional data are included in the figure.   It is apparent that the mixture with the high-

[45] Phil. Trans., 151, 205 (1861).

[46] Trans. Faraday Soc., 26, 642 (1930); cf., also, Bonnell: Trans. Faraday Soc., 29, 1221 (1933); Kröger and Fischer: Kolloid-Z., 47, 10 (1929).

est silica concentration, which sets the quickest, starts to synerize the soonest and exudes the most liquid. If the first portion of the curves are plotted on a larger scale, they are found to be S-shaped, indicating that the process is autocatalytic.

The initial velocity of syneresis is greater the more alkaline the jelly, but the total volume synerized is greater from the acid jelly. Under otherwise constant conditions, the rate of syneresis is greater the higher the temperature, the velocity being approximately doubled for each rise of 10°.

Since the jelly-formation process consists in the coagulation of the hydrous particles of silica into an enmeshing network, the syneresis which follows the initial set is the visible manifestation of further slow coagulation and agglomeration which squeezes out some of the entangled liquid. Thus the more rapid the set, the shorter is the induction period and the greater is the initial velocity of syneresis. Moreover, those factors which accelerate the setting process increase the rate of syneresis. Finally, the process is autocatalytic just as is the process of slow coagulation in cases where jellies are not ordinarily produced.[47]

Silica jellies will split rhythmically[48] during syneresis provided the shrinkage is sufficient to cause any splitting and provided the initial splitting occurs along some line which does not coincide with the inside circumference of the tube or one of its diameters. The phenomenon is general when the tube containing the jelly is set out of the vertical position, since the split starts at the top off center, owing to the lack of symmetry of the meniscus.

Reactions in Silica Jelly

On account of the ease with which electrolytes diffuse into silica jellies, a number of interesting reactions have been carried out in this medium. For example, Hatschek and Simon[49] prepared large gold crystals by reducing gold salts with several reducing agents; Simon grew a lead "tree," consisting of large irregular crystals of lead, by placing a small piece of zinc in the jelly containing lead nitrate or acetate;[50] and Holmes[51] prepared magnificent crystals of a num-

[47] Freundlich: "Kapillarchemie," 2, 161 (1932).

[48] Davies: J. Phys. Chem., 35, 3618 (1931); cf. Eversole and Doughty: J. Am. Chem. Soc., 56, 1263 (1934).

[49] J. Soc. Chem. Ind., 31, 439 (1912); Mining Eng. World, 37, 280 (1912); cf. Hatschek: Kolloid-Z., 10, 77 (1912).

[50] Simon: Kolloid-Z., 12, 171 (1913); for details see Taft and Stareck: J. Chem. Ed., 7, 1520 (1930).

[51] J. Phys. Chem., 21, 709 (1917).

ber of metals and salts. The jelly prevents rapid mixing of the inter-acting solutions, thereby avoiding rapid precipitation and the con-sequent formation of amorphous particles or small crystals.

Silica jelly is an excellent medium in which to form rhythmic bands or Liesegang rings. Mukherjee and Chatterji[52] list a large number of salts that form bands in this jelly. They distinguish two types of salts: one type forms sharp bands with a clear zone between, and a second type forms alternate layers of coagulated and peptized compound which are not sharply defined. The theory of the banding process has been taken up on pages 24 and 180.

The varicolored bands of gold in silica described by Holmes[53] are obtained only in changing light and are not true Liesegang rings; in the dark, large crystals only are formed.[54]

The importance of reactions in silica jelly has already been mentioned (p. 26).

SILICA GEL

FORMATION AND ACTIVATION

The product commonly called silica gel is the adsorbent prepared by drying silica jelly under suitable conditions. Patrick's[55] method of preparing the gel consists in pouring silicate of soda of about 1.185 sp. gr. into an equal volume of 10% HCl at 50° under violent agitation. After setting, the resulting jelly is broken up and washed with hot water and dried. It makes little difference whether the sodium chloride is washed out before or after the drying.[56] The rate and conditions of drying determine the porosity of the gel, and at the outset, the process is carried out slowly. A temperature of 75–120° is first employed, followed by raising the temperature grad-ually to 300°. Patrick and Greider[57] state that the most active samples are obtained by heating at 250–300° in vacuo for a half-hour or more. Later, Patrick, Frazer, and Rush[58] showed that the adsorption capacity of the gel for carbon tetrachloride is not decreased appreciably unless the temperature is raised above 750°. This was confirmed by Holmes and Elder[59] for the adsorption of benzene by

[52] Kolloid-Z., 50, 147 (1930); Lincoln and Hillyer: J. Phys. Chem., 38, 907 (1934).
[53] J. Am. Chem. Soc., 40, 1187 (1918).
[54] Davies: J. Am. Chem. Soc., 44, 2700 (1922); 45, 2261 (1923).
[55] U. S. Pat. 1,297,724 (1919).
[56] Fells and Firth: J. Phys. Chem., 29, 241 (1925).
[57] J. Phys. Chem., 29, 1031 (1925).
[58] J. Phys. Chem., 31, 1511 (1927).
[59] J. Phys. Chem., 35, 82 (1931).

the gel. If the heat of wetting by water is taken as the measure of the activity of the gel, Bartell and Almy[60] showed that the temperature of heating should be in the neighborhood of 300° for the maximum activity. The time of heating is immaterial provided a minimum of 30 minutes is observed.

Since the water content of the gel is decreased by heating to temperatures above 300°, it is not obvious why the gel with lower water content has a lower heat of adsorption. To account for this, Bartell and Almy consider that the water present in the gel before activation is not all held in the same manner. A part is apparently held in relatively large capillary spaces. This is easily removed by moderate heat treatment, thereby increasing the activity as measured by the heat of wetting. The remainder is "bound" much more firmly, apparently in such minute capillaries or ultra-pores that the binding forces are those of adhesion rather than cohesion.[61] Removal of water from these pores causes the structure to collapse partially, thereby decreasing the effective surface and the activity. By ignition at high temperatures the adsorption capacity for water is reduced to zero.[62]

Since the properties of silica gel are influenced to a marked degree by the method of preparation, various attempts have been made to improve on the gel covered by Patrick's patent. Briggs[63] dried the unwashed gel containing sodium chloride at 300° and plunged it while still hot into hot distilled water. After washing by decantation, the gel was dried again at 300° and the process repeated until all the chloride was removed. The adsorption capacity of this gel for nitrogen at −190° was 60% greater than that of a good grade of adsorbent charcoal. Holmes and Anderson[64] added dilute ferric chloride to water glass until neutrality was reached, dried the gelatinous precipitate, and then dissolved out the hydrous ferric oxide with hydrochloric acid, leaving a white, highly porous gel. Such a gel will adsorb 62% of its weight of benzene compared with 32.2% for a Patrick gel. For increasing the adsorptive capacity, Holmes, Sullivan, and Metcalf[65] stopped the initial slow drying at approximately 60%,

[60] J. Phys. Chem., **36**, 475 (1932).

[61] *Cf.* Fells and Firth: J. Phys. Chem., **31**, 1230 (1927); Jones and Gortner: **36**, 387 (1932).

[62] Van Bemmelen: Arch. Néerland sci., **6** II, 607 (1901).

[63] Proc. Roy. Soc. (London) **100A**, 88 (1921); *cf.* Fells and Firth: J. Phys. Chem., **29**, 241 (1925).

[64] Ind. Eng. Chem., **17**, 280 (1925).

[65] Ind. Eng. Chem., **18**, 386 (1928).

allowed the partly dried gel to synerize for a week or two in a closed vessel, and then treated it with boiling dilute acid for a few hours before the washing and final drying.[66]   In this way was prepared a "gel from iron" which adsorbed 126% of its weight of benzene, and later, one which adsorbed 140% of its weight of benzene.   Nickel chloride or other heavy metal salts may be substituted for ferric chloride in the Holmes process.   Thus, using copper sulfate, Holmes and Elder[59] obtained a gel which would adsorb up to 156% of its weight of benzene.   In Fig. 36 are summarized some observations of Holmes and Elder[59] which show the relative adsorption capacity
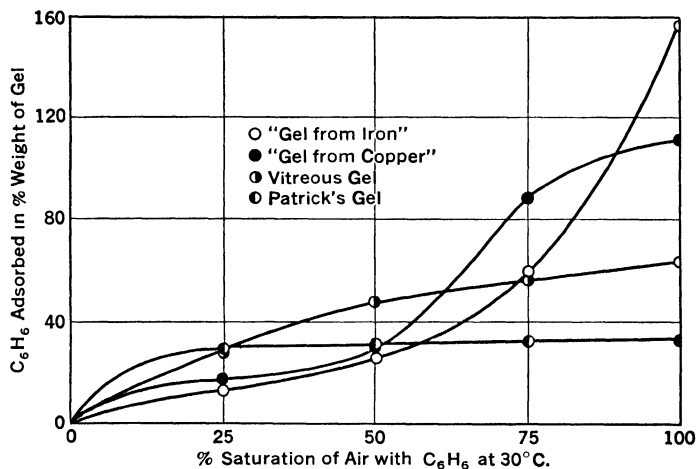
FIG. 36.—Adsorption of C_6H_6 vapors by silica gels prepared in different ways.

for benzene vapors of gels prepared by different methods.   These data indicate the superior adsorption capacity for benzene of Holmes' chalky gels.   Elder and Brandes[67] showed, however, that Patrick's gel is superior to the chalky gel as an adsorbent for water and ethyl acetate vapors at low partial pressures but not at relatively high partial pressures.

ADSORPTION BY SILICA GEL

Adsorption of Gases and Vapors

The Capillary Theory of Adsorption.   The adsorption of gases and vapors by silica gel has been studied in detail by Patrick and his

[66] *Cf.* Holmes: "Laboratory Manual of Colloid Chemistry," 195 (1928).
[67] J. Phys. Chem., **35**, 3022 (1931).

collaborators. In his first work along this line, adsorption isotherms for sulfur dioxide were obtained at varying temperatures between -80 and $+100°$.[68] The empirical equation of Freundlich,

$$x/m = kP^{1/n} \tag{1}$$

where x is the amount adsorbed by the mass of adsorbent m at pressure P, and k and n are constants, was found to hold over almost the entire range studied, exceptions being at points where the saturation pressure was approached.[69] The straight lines obtained by plotting logarithm x/m against logarithm P at various temperatures were separated widely.

Patrick considers the adsorption by a porous substance, such as silica gel, to be a capillary condensation that is independent of the chemical nature of the adsorbent. Capillary adsorbents differ, therefore, in the extent of their total internal volume and also in the dimensions of the pores that make up the internal volume. If such be the case, the form of the adsorption isotherm merely expresses the distribution of the internal volume as a function of the dimensions of the pores. From this point of view, it would appear logical to seek a relation between the volume occupied by the adsorbed gas and the equilibrium pressure rather than between the weight of adsorbed gas and the pressure. As a matter of fact, when the logarithms of the volume V of liquid sulfur dioxide (obtained by dividing the weight of adsorbed gas by the density of liquid sulfur dioxide at the corresponding pressure) are used as ordinates, the curves are brought closer together. The next step is to plot logarithm V against logarithm of the "corresponding pressure" P/P_0, where P_0 is the vapor pressure of the condensed gas at the temperature in question. In this way it was found that greater volumes were taken up at lower temperatures at the same partial pressures, probably because the condensed phase is more compressible at the higher temperatures, the surface tension being smaller.[70] As an empirical relationship, dividing the volume of condensed sulfur dioxide by the value of the surface tension σ, raised to a fractional power, gives a correction in the right direction. The Freundlich equation thus takes the form

$$\frac{V}{\sigma^{1/n}} = k\left(\frac{P}{P_0}\right)^{1/n} \tag{2}$$

[68] Patrick and McGavack: J. Am. Chem. Soc., **42**, 946 (1920); *cf.* Bosshard and Jaag: Helv. Chim. Acta, **12**, 105 (1929).

[69] *Cf.* Ray: J. Phys. Chem., **29**, 74 (1925).

[70] Patrick and McGavack: J. Am. Chem. Soc., **42**, 976 (1920).

or assuming the same value of $1/n$ to hold for P/P_0 and σ,

$$V = k\left(\frac{P\sigma}{P_0}\right)^{1/n} \qquad (3)$$

This equation appears to be a general one for capillary adsorbents[71] and has been applied by Patrick and his pupils to the adsorption of sulfur dioxide, butane,[72] benzene, carbon tetrachloride, alcohol,[73] and ammonia,[74] after correcting for the amount dissolved in the gel water.[75]

Since adsorption of gases takes place above the critical temperature where no condensation to liquid occurs under ordinary conditions, Patrick, Preston, and Owen[76] studied the adsorption of carbon dioxide and nitrous oxide in the region of the critical temperature. When equation (3) was applied to the experimental results, it was found that k at $0°$ was not equal to k at higher temperatures near the critical point. This variation in k was attributed to an increase in surface tension of the liquid in the capillaries at temperatures near the critical temperature, owing to capillary forces. After correcting the surface tension, the equation was found to apply, indicating that in all cases the constants k and $1/n$ depend only on the structure of the silica gel. Since the theory applies even above the critical temperatures for carbon dioxide and nitrous oxide on a plane surface, Patrick suggests that the critical temperature is raised in the pores of the gel.

Adsorption of the Halogens. Reyerson and Cameron[77] made precise measurements of the adsorption and desorption of bromine and iodine on both silica gel and activated charcoal in an all glass-quartz system. Their data for bromine on silica gel are shown graphically in Fig. 37. The curves for iodine on silica gel are similar to those for bromine but the adsorption of the latter is tenfold greater than that of the former. Except for the highest desorption of bromine at $79°$, the adsorption and desorption phenomena are completely

[71] Munro and Johnson [J. Phys. Chem., **30**, 172 (1926)] found the equation to hold for the adsorption of water vapor by alumina except when the partial pressure approaches the vapor pressure of the liquid at the temperature of the adsorbent.

[72] Patrick and Long: J. Phys. Chem., **29**, 336 (1925).

[73] Patrick and Opdyke: J. Phys. Chem., **29**, 601 (1925).

[74] Davidheiser and Patrick: J. Am. Chem. Soc., **44**, 1 (1922); cf. Magnus and Kieffer: Z. anorg. Chem., **179**, 215 (1929).

[75] Cf. Neuhausen and Patrick: J. Phys. Chem., **25**, 693 (1921).

[76] J. Phys. Chem., **29**, 421 (1925).

[77] J. Phys. Chem., **39**, 181 (1935); cf. Bosshard and Jaag: Helv. Chim. Acta, **12**, 105 (1929).

reversible.   The data do not fit either the Freundlich equation or the Langmuir equation (Vol. I, p. 197) but they can be represented quite well by the Patrick equation.   This suggests that the vapors are held by silica gel in a rather loose type of physical binding or by capillary condensation.   On the other hand, the data for adsorption of the halogens on charcoal follow the Langmuir equation closely, indicating monomolecular adsorption on the charcoal surface.
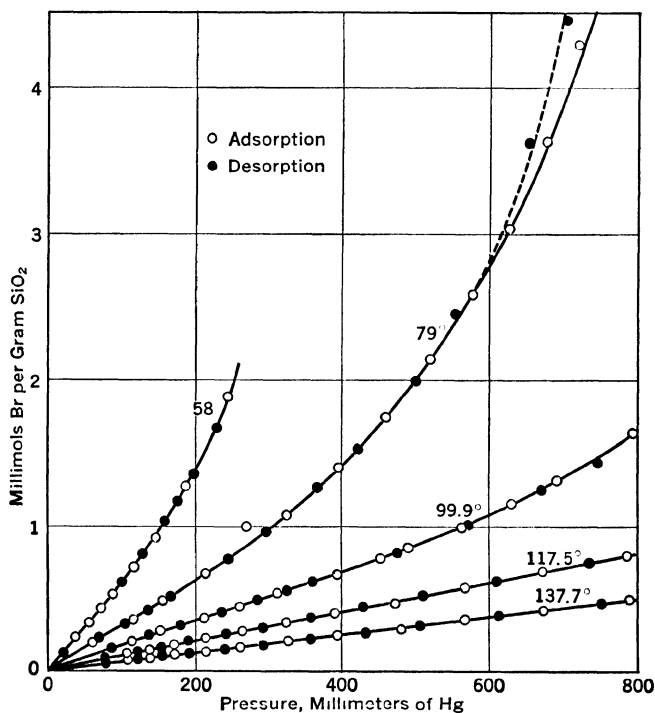
FIG. 37.—Adsorption and desorption of bromine on silica gel.

The adsorption of chlorine by silica gel has been studied by Magnus and Müller.[78]

Limitations of the Capillary Theory of Adsorption.   As a result of a study of the adsorption of helium, argon, oxygen, and methane between −183 and 0°, Urry,[79] in Patrick's laboratory, pointed out definite limitations in the applicability of the capillary theory of adsorption.   Urry believes that the adsorption of a gas on the gel takes place in at least two ways.   With every gas a discontinuity has

[78] Z. physik. Chem., **A148**, 241 (1930).
[79] J. Phys. Chem., **36**, 1831 (1932).

been observed in the adsorption phenomena at some definite tempera-
ture which is probably close to the critical temperature of the gas in the
capillaries of the gel.   Above the discontinuity, the adsorption is a
surface phenomenon only, the adsorption volume being proportional
to the pressure.   Below the discontinuity, both surface and capillary
adsorption may be considered to occur.   In any event, it is possible to
separate the two phases of adsorption by making certain assumptions
and to apply the Patrick equation to that part which is considered to
be capillary adsorption.

Although something may be gained by distinguishing between the
surface adsorption and the adsorption which may be expressed by the
Patrick equation, most people do not make this distinction even with
an inert adsorbent such as silica; and capillary condensation is not
generally believed to play much of a rôle in adsorption by such polar
adsorbents as activated charcoal.[80]

The discontinuity in the adsorption of gases in the neighborhood
of the critical temperature is easy to understand.   It is not obvious,
however, why the adsorption of vapors of such compounds as carbon
tetrachloride and benzene should take place in a stepwise fashion
throughout a wide range of pressures when special attention is paid to
the displacing of most of the water from the gel before beginning the
adsorption study.[81]

Miscellaneous Observations.   Alyea[82] observed a large activated
adsorption of hydrogen by Pyrex vessels at temperatures above 500°.
Silica gel, on the other hand, does not adsorb hydrogen at any temper-
ature between 400 and 600°.[83]

Silica gel adsorbs radon much more strongly than does Pyrex.[84]
The adsorption is greatest if the water content is between 1.2 and 5.5%,
whereas above 40 and below 1.2% water, the adsorption falls off
rapidly.   Moreover, the adsorption is much less for an aged gel than
for a freshly formed one.[85]

[80] Chaney: Trans. Am. Electrochem. Soc., **36**, 91 (1919); Trans. Am. Inst. Chem.
Engrs., **15** I, 292; Chaney, Ray, and St. John: 309 (1923); Wilson: Phys. Rev. (2) **16**,
8 (1920); see Coolidge [J. Am. Chem. Soc., **48**, 1795 (1926)] for criticism of the capil-
lary theory of adsorption.

[81] Allmand and Burrage: Proc. Roy. Soc. (London) **130A**, 610 (1931); Allmand,
Burrage, and Chaplin: Trans. Faraday Soc., **28**, 218 (1932); Burrage: J. Phys. Chem.,
37, 33, 735 (1933).

[82] J. Am. Chem. Soc., **53**, 1324 (1931).

[83] Reyerson: J. Am. Chem. Soc., **55**, 3105 (1933).

[84] Reyerson: J. Phys. Chem., **37**, 534 (1933).

[85] Francis: Kolloid-Z., **59**, 292 (1932); cf. Becker and Stehberger: Ann. Physik (5)
1, 529 (1929).

Extending Langmuir's theory of adsorption to the case of gas mixtures, Markham and Benton[86] deduce that each gas in a binary mixture should be adsorbed less than if it were present alone at the same partial pressure. With mixtures of carbon monoxide and oxygen, a rough agreement exists between the calculated and observed adsorptions, whereas with mixtures containing carbon dioxide, the observed values are not only greater than the calculated, but, in many cases are greater in the presence of the second gas than in its absence. The reason for this is not obvious. Magnus and Grähling[87] studied the simultaneous adsorption of oxygen and ozone on silica gel at temperatures between -69 and $-49°$.

The heat of adsorption of various gases in calories per mol at $0°$ obtained by Kälberer and Schuster[88] is as follows: $A = 2500–3200$; $CO_2 = 7200$; $N_2 = 3000$; $C_2H_4 = 7300–7700$. The adsorption volume was found to be a function of the heat of adsorption, being smaller the higher the heat of adsorption.

Adsorption of Liquids

Adhesion Tension. When a liquid is adsorbed by a solid it forms a liquid film on the solid and the liquid is said to wet the solid. Bartell and his students[89] have carried out extensive investigations on the nature of wetting and the phenomena involved in the wetting of solids by liquids. Wetting is defined as the phenomenon which occurs when a solid phase and a liquid phase come in contact in any manner so as to form a solid-liquid interface. The degree of wetting means the amount of change in free surface energy or the amount of work done when the solid and liquid are brought together. The degree of wetting is best expressed in terms of the adhesion tension solid-liquid which is given by the expression:[90]

$$A_{12} = S_1 - S_{12} = S_2 \cos \theta_{12} \ [91]$$

if the solid is not wet sufficiently to displace all the air and hence

[86] J. Am. Chem. Soc., **53**, 497 (1931).

[87] Z. physik. Chem., **A145**, 27 (1929).

[88] Z. physik. Chem., **A141**, 270 (1929). For the heat of adsorption of NH_3, CH_3NH, $(CH_3)_2NH$, and $(CH_3)_2N$ *see* Felsing and Ashby: J. Am. Chem. Soc., **56**, 2226 (1934).

[89] Bartell and Osterhof: Ind. Eng. Chem., **19**, 1277 (1927); Colloid Symposium Monograph, **5**, 113 (1928); Bartell and Merrill: J. Phys. Chem., **36**, 1178 (1932); Bartell: Alexander's "Colloid Chemistry," **3**, 41 (1931).

[90] Young: Phil. Trans., **95**, 65 (1805); Freundlich: "Colloid and Capillary Chemistry," 157 (1926).

gives a definite contact angle.   If the contact angle is zero,the adhesion tension is given by the following expression formulated by Bartell:

$$A_{13} - A_{12} = S_{12} - S_{13} = S_{23} \cos \theta_{23} \,[91]$$

Some observations of adhesion tensions of liquids against silica gel are given in Table XVI. The notations "pressure of displacement method"

TABLE XVI

ADHESION TENSION VALUES A_{12} OF LIQUIDS AGAINST SILICA

Liquids	A_{12}	
	Pressure of displacement method	Microscopic method
Water.............	82.82	75.92
Butyl acetate.......	73.45	66.60
Carbon tetrachloride.	40.69	35.67
Toluene...........	54.70	46.54
Benzene...........	52.43	45.43
Carbon bisulfide.....	45.94	40.46

and "microscopic method" refer to two different methods used for determining contact angles.   It is apparent that the two methods give values which are quite comparable considering that the samples of silica were not the same.   This indicates that the adhesion tension of a liquid for a solid, which is a measure of the degree of wetting or adsorption, is a specific and definite property of the system.

Bartell has used adhesion tension measurements to advantage in determining the degree of wetting of crude petroleum oils by silica[92] and for the evaluation of the so-called "liquid absorption" of organic liquids, oils, etc., by powdered solids such as pigments.[93]

Heat of Wetting.   The wetting of a liquid by a solid is accompanied by an evolution of heat which is called the heat of wetting.

[91] S_1 = surface tension of the solid; S_2 = surface tension of organic liquid; S_{12} = interfacial tension of organic liquid vs. solid; S_{13} = interfacial tension water vs. solid; S_{23} = interfacial tension water vs. organic liquid; A_{12} = adhesion tension organic liquid vs. solid; A_{13} = adhesion tension water vs. solid; θ_{12} = liquid-air-solid contact angle; θ_{23} = interfacial contact angle between liquid-liquid interface and solid.

[92] Bartell and Miller: Ind. Eng. Chem., **20**, 738 (1928); cf., also, **24**, 335 (1932).

[93] Bartell and Greager: Ind. Eng. Chem., **21**, 1248 (1929).

This was first determined for a number of liquids with silica gel by Patrick and Grimm,[94] who pointed out that the observed values could be accounted for on the basis of surface energy changes. These observations have been confirmed and extended by Bartell and Fu[95] using a specially prepared silica gel containing 4% water and an almost anhydrous oxide obtained by ignition of the gel. From the heat of wetting, $-Q$, the adhesion tension solid-liquid, A, and the change in surface tension with change in temperature, dS/dT, Bartell and Fu calculated the specific surfaces area, a, using the following equation:[96]

$$a = \frac{-Q}{A - KT\dfrac{dS}{dT}}$$

in which K is a constant for the given solid-liquid system. The data summarized in Table XVII show very good agreement for the specific surface area values of both the anhydrous and hydrous silica using

TABLE XVII

Heat of Wetting and Surface Area of Anhydrous and Hydrous Silica

Adsorbent	Liquid	A	$-Q$ calories/g	a cm²/g
SiO₂...........	Water	82.82	15.91	5 × 10⁶
	Benzene	42.43	12.66	4.3 × 10⁶
	Chloroform	59.95	14.52	4.5 × 10⁶
	Nitrobenzene	63.45	12.3	4.5 × 10⁶
	Carbon tetrachloride	40.7	10.0	4.3 × 10⁶
			Average	4.5 × 10⁶
SiO₂ + 4% H₂O	Ethyl alcohol	......	26.9	7 × 10⁶
	Acetone	......	26.9	7.2 × 10⁶
	Water	......	24.31	7.5 × 10⁶
	Benzene	......	21.5	7.3 × 10⁶
			Average	7.25 × 10⁶

[94] J. Am. Chem. Soc., **43**, 2144 (1921); cf. Grimm, Raudenbusch, and Wolff: Z. angew. Chem., **41**, 104 (1928).

[95] Colloid Symposium Annual, **7**, 135 (1930); cf. Harkins and Dahlstrom: Ind. Eng. Chem., **22**, 897 (1930).

[96] Cf., also, Williams: Proc. Roy. Soc., Edinburgh, **38**, 24 (1917–8); Harkins and Ewing: J. Am. Chem. Soc., **43**, 1787 (1921); Bartell and Osterhof: Z. physik. Chem. (Cohen-Festband) A130, 715 (1927).

different liquids. With both samples the value with water is a little high since even the so-called anhydrous sample contained a little water which would not be displaced by the organic liquids having a lower adhesion tension. Since the heat of wetting depends on the extent of surface actually brought in contact with the liquid, the smaller values with the organic liquids would be expected if some of the surface was already occupied by water.

Adsorption of Liquids from Solution

Over a Limited Range of Concentration. Adsorption from solution by silica gel was investigated in Patrick's[97] laboratory for the
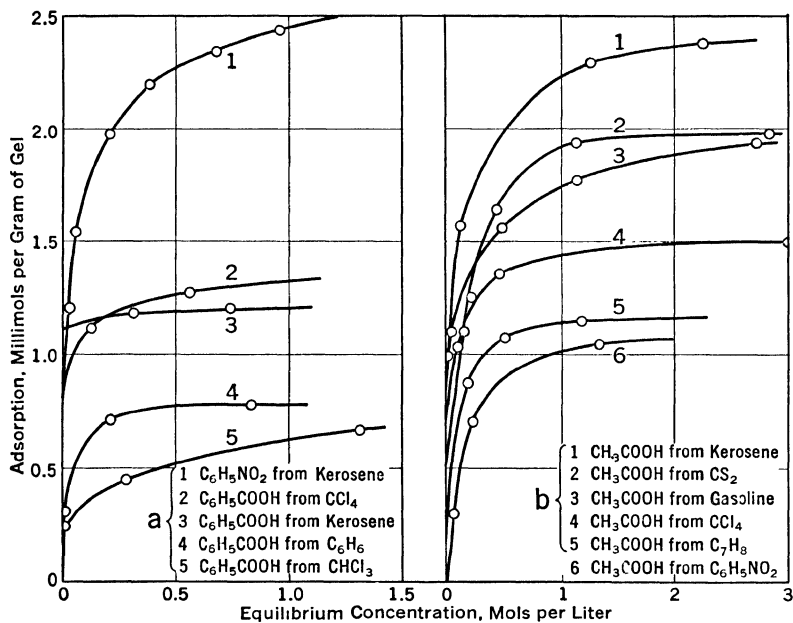
FIG. 38.—Adsorption by silica gel.

following systems: formic acid, butyric acid, acetic acid, benzoic acid, and iodine from a series of solvents; nitrobenzene from kerosene; and acetic acid from carbon bisulfide. A few of the results are reproduced in Fig. 38.

In general, Patrick finds the adsorption of a solute to increase as its solubility in the solvent decreases. For example, the adsorption of benzoic acid from the several solvents is in inverse order of its

[97] Patrick and Jones: J. Phys. Chem., **29**, 1 (1925).

solubility in these solvents. Similarly, formic acid is much more strongly adsorbed from toluene than is the more soluble butyric acid; iodine is adsorbed to a small extent in accord with the same laws. Moreover, nitrobenzene is adsorbed to a very great extent from kerosene, with which it is only partially miscible, whereas benzene, which is much closer to kerosene in the solubility series, is adsorbed to a considerably smaller extent.

Contrary to Freundlich's[98] view that very little adsorption would be expected to take place from organic solvents which have a relatively low surface tension, it is evident that adsorption does take place to a very marked degree and that the amount adsorbed bears no relation to the surface tension of the solvent. Thus, the greatest adsorption of acetic acid occurs from benzene solution, and becomes less and less from the following solvents in order: carbon bisulfide, gasoline, carbon tetrachloride, toluene, and nitrobenzene; whereas the surface tensions of these substances, respectively, are: 32, 15, 25, 29, 43. The same order of solvents holds in the adsorption of the other acids investigated.

It is sometimes stated that, if a liquid with a high heat of wetting is used as a solvent, less adsorption of the solute will take place from that solution.[99] This generalization is likewise incorrect, as pointed out by Bartell and Fu.[95] The question as to whether a liquid will be strongly or slightly adsorbed depends in the first instance on its adhesion tension against the solid. As shown in Table XVII, a liquid with a lower adhesion tension may have a higher heat of wetting than one with a greater adhesion tension. The reason is that heat of wetting is the measure of the decrease of total surface energy and not of the free surface energy. If a liquid be taken as solvent with a high adhesion tension relatively to the solute, the adsorbent will take up so much of the solvent that the adsorption of the solute will be low. On the other hand, if a liquid with a high heat of wetting instead of a high adhesion tension is taken as solvent, a corresponding behavior may not result. Thus Bartell and Fu point out that silica gel adsorbs better from acetone than from water solutions, and carbon adsorbs better from nitrobenzene than from alphabromnaphthalene solutions, in spite of the fact that the first-mentioned liquid in the two pairs has the higher heat of wetting.

Over the Entire Concentration Range. In a systematic study of adsorption from non-aqueous binary systems over the entire concen-

[98] "Kapillarchemie," 2nd ed., 259 (1922).
[99] Berl and Wachendorff: Kolloid-Z. (Zsigmondy Festschrift) **36**, 36 (1925).

tration range, Bartell[100] showed that the component having the higher adhesion tension against the solid is preferentially adsorbed over the greater portion of the concentration range.   Another factor determining the relative adsorption of the two components is the solubility of the adsorbate in the solvent.   These relationships are brought out in Fig. 39, which shows the adsorption of various alcohols from benzene throughout the entire range of concentrations.   The adsorption is expressed as $H(x_0 - x)/m$, in which H is the total number of millimols that make up the solution and x_0 and x are the mol fractions of solute present before and after adsorption, respectively.   The alcohols have similar adhesion tensions against silica which are higher
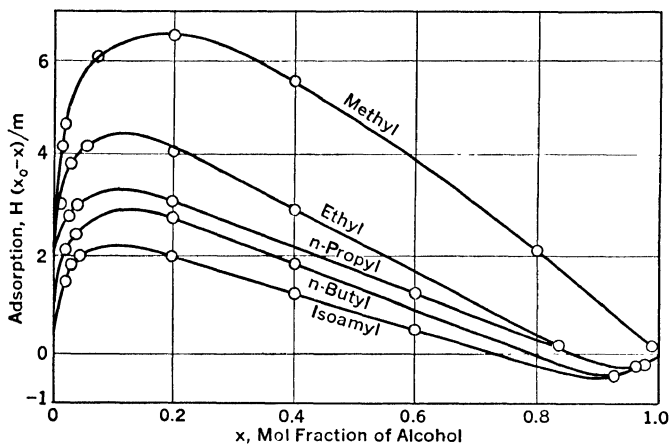
FIG. 39.—Adsorption by silica gel of alcohols from benzene solution throughout the entire range of concentrations.

than that of benzene.   Accordingly, the adsorption of all the alcohols is positive throughout most of the concentration range, but the least soluble one is adsorbed the most.

The adsorption from binary mixtures can be expressed over the entire range by a modified form of Freundlich's equation which expresses the measure of adsorption in terms of change in concentration (Vol. I, p. 299):

$$H\Delta x/m = \alpha x^n(1 - x) - \beta(1 - x)^a x$$

In general, the order of increasing adhesion tension values of a series of liquids against carbon is the reverse of the order of increasing

[100] Bartell, Scheffler, and Sloan: J. Am. Chem. Soc., **53**, 2501, 2507 (1931); cf. Rao: J. Phys. Chem., **36**, 616 (1932); Jones and Outridge: J. Chem. Soc., 1574 (1930).

values against silica.   Accordingly, one might expect the adsorption effects with carbon as adsorbent to be, at least qualitatively, the reverse of the effects obtained with silica.   This was confirmed by Bartell in studies of the adsorption from the benzene-ethyl alcohol system using both carbon and silica as adsorbents.   With carbon, the non-polar liquid benzene was much more highly adsorbed than the polar liquid alcohol, and the former was adsorbed preferentially over the greater portion of the concentration range.   On the other hand, with the more polar adsorbent silica, the polar liquid alcohol is more highly adsorbed than the benzene over a greater portion of the concentration range.   Similarly, Holmes and McKelvey[101] found the order of adsorption of the fatty acids from solutions in the non-polar solvent toluene by silica gel to be: acetic > propionic > butyric > caprylic, which is the reverse of the order of adsorption of the acids from aqueous solution by carbon.   Oriented adsorption is a factor in this process.   In general, when a liquid is brought in contact with silica, the molecule is oriented so that the more polar group is in contact with the silica; and the reverse is true with carbon.   Accordingly, a liquid which gives a high adhesion tension with carbon gives a low adhesion tension with silica.   In the adsorption of the fatty acids on silica from toluene solution, the highly polar carboxyl group is oriented toward the silica surface and the non-polar alkyl group toward the solvent.   Since the polarity falls off with increasing molecular weight in the fatty acids series, the lower members of the series are the more strongly adsorbed or have a higher adhesion tension against silica than the higher members.[102]   The order of adsorption of the fatty acids is the same from aqueous as from toluene solutions, but the amount of adsorption from aqueous solutions is very much less.[103]

Grimm and Wolff[104] studied the most favorable conditions for separating binary mixtures by preferential adsorption on silica gel. Water may be preferentially adsorbed from alcohol by means of silica gel.[105]

Capillary Theory of Adsorption.   Adsorption from solution is believed by Patrick to involve capillary forces rather than surface forces.   He suggests that the adsorption results from a phase separation in the capillaries caused by preferential wetting of the pores by

[101] J. Phys. Chem., **32**, 1522 (1928).

[102] *Cf.*, *also*, Holmes and Thor: Colloid Symposium Annual, **7**, 213 (1930).

[103] Bartell and Fu: J. Phys. Chem., **33**, 676 (1929).

[104] Z. angew. Chem., **41**, 98; Grimm, Raudenbusch, and Wolff: 103 (1928).

[105] Davis and Swearingen: J. Phys. Chem., **35**, 1308 (1931).

the solute, followed by the production of highly concave surfaces of solute which effects a lowering of solubility of solute in the solvent. For example, when a solution of acetic acid in sulfur dioxide is brought in contact with silica gel, the acetic acid preferentially wets the gel, the pores of which fill up with a phase rich in acetic acid owing to the marked concave curvature that this phase presents to the body of the solution.   In other words, although acetic acid is miscible with carbon bisulfide in all proportions when the surfaces are plain, this is not the case if the curvatures of the separating surfaces are sufficiently concave.

This interpretation of adsorption from solution is analogous to the mechanism proposed by Patrick to explain adsorption from the gas phase.   In the latter, the adsorption or condensation in capillaries at pressures lower than the saturation pressure at the given temperature is accounted for by assuming that the pores of the gel are presented to the main body of the gas.   The empirical formula (3) which satisfactorily explains the adsorption of gases by silica gel has been changed in order to apply it to adsorption from solution.[106]   The modified equation is

$$V = k\left(\frac{S\sigma}{S_0}\right)^{1/n} \tag{4}$$

where V is the volume of liquid solute adsorbed per gram of gel, σ is the interfacial tension, S the equilibrium concentration of the solute in the surrounding solvent, and S_0 the "solubility." Since S_0 is analogous to P_0 in equation (3), it might be taken to represent the ordinary maximum solubility of the solute in the solvent at the given temperature.   But if this were true, S_0 would be infinity for completely miscible liquids, whereas it has been found always to have a finite value. By applying equation (4) to adsorption from solution, in several cases, S_0 has been calculated to be always less than the ordinary solubility. S_0 is therefore defined as the dissolving power of the solvent as uninfluenced by molecules of the solute subsequently entering.

Whatever merit the above theory may have, Patrick and his pupils are almost alone in subscribing to it.

Adsorption of Solids from Solution

Owing to the strong preferential adsorption of silica gel for bases, alkali salts of organic acids undergo hydrolytic adsorption from

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[106] Patrick and Eberman: J. Phys. Chem., **29**, 220 (1925).

aqueous solution[107] (Vol. I, p. 292) in increasing amounts in the order: formate < acetate < propionate < butyrate. The hydrolytic adsorption of inorganic salts such as potassium chloride is slight, and there is no salt adsorption as such.[108] With alkali salts in the presence of ammonium hydroxide the alkali hydroxide is adsorbed.

As already noted, organic acids are adsorbed but slightly from aqueous solutions by silica, and Bartell and Fu[95] observed little or no adsorption of inorganic acids by a gel containing 4% water.[109] Mukherjee[110] claims that acids are strongly adsorbed if the gel is properly prepared, but he was working with gels that contained up to 85% water.

Inorganic bases are strongly adsorbed by silica gel in the order: LiOH > NaOH, KOH > NH₄OH.[103] Kolthoff and Stenger[111] showed that it is impossible to determine the adsorption of such alkalis with any degree of exactness on account of the dissolving effect on the gel.[112] Potassium salts cut down the adsorption of potassium hydroxide, whereas ammonium salts have little effect on the adsorption of ammonia. With mixtures containing ammonium and potassium ions, the total base adsorption is a function of the hydroxyl ion concentration and the ratio in which the bases are adsorbed is determined mainly by the ratio of potassium to ammonium in the solution. The adsorption of calcium ion and copper ammonium ion from ammoniacal solution first increases and then decreases with the ammonia concentration. The initial increase is due to increasing adsorption of the hydroxyl ion, and the subsequent decrease results from the cutting down of the adsorption of the bivalent cations by the adsorption of ammonium. The complex ions of copper and nickel adsorbed on silica gel are readily reduced to metal by hydrogen.[113]

The adsorption of a series of 18 organic compounds of various kinds by silica gel was found to be roughly proportional to their basic strength.[114] Similarly, the adsorption of dyes is a function of the basicity of the dye.[115]

[107] Bartell and Fu: J. Phys. Chem., **33**, 676 (1929); Mukherjee, Ghosh, Krishnamurti, Ghosh, Mitra, and Roy: J. Chem. Soc., 3023 (1926).

[108] *Cf.* Berthon: Compt. rend., **195**, 43, 384 (1932).

[109] *Cf.* Lakhani: Proc. 15th Indian Sci. Congress, 134 (1928).

[110] Mukherjee, Ghosh, Krishnamurti, Ghosh, Mitra, and Roy: J. Chem. Soc., 3023 (1926); Mukherjee: Nature, **115**, 497 (1925).

[111] J. Phys. Chem., **36**, 2113 (1932); **38**, 249 (1934).

[112] *Cf.* Patrick and Barclay: J. Phys. Chem., **29**, 1400 (1925).

[113] Smith and Reyerson: J. Am. Chem. Soc., **52**, 2584 (1930).

[114] Grettie and Williams: J. Am. Chem. Soc., **50**, 668 (1928).

[115] Birutovich: Kolloid-Z., **44**, 239 (1928).

APPLICATIONS

Silica gel has several desirable properties which render it of value as a technical adsorbent. First of all, it possesses a strong adsorptive capacity for vapors and liquids.[116] Moreover, it is quite inert, and the adsorbed liquids can be driven off and recovered if desired, simply by heating the gel, leaving the latter reactivated and ready to use over again.[117]

Because of its capacity to adsorb compounds of sulfur, silica gel has been suggested to remove such compounds from crude petroleum distillates and from light oils recovered during the manufacture of coal gas and water gas, in place of the usual sulfuric acid treatment which has the disadvantage of taking out desirable unsaturated hydrocarbons. As an indication of the relative ability of various commercial adsorbents to remove sulfur compounds from a Mexican crude kerosene distillate, the results reported by the Silica Gel Corporation[118] are given in Fig. 40. These data indicate that the adsorption capacity of silica gel for sulfur compounds is very much greater than that of the other commercial adsorbents. Although the gel has been used successfully as a desulfurizing agent[119] in certain cases, it is apparently unsatisfactory in most.[120]

FIG. 40.—Adsorption of sulfur compounds from crude kerosene distillate by various adsorbents.

1 Infusorial Earth
2 Precipitated Silica
3 Bone Black
4 Fuller's Earth
5 Death Valley Clay
6 Activated Cocoanut Charcoal
7 Silica Gel

Sulfur Content of Filtered Oil, Percent

Grams Filtered Oil through 100 Grams of Adsorbent

[116] Patrick, Lovelace, and Miller: U. S. Pat. 1,335,348 (1920).

[117] Cf. Taylor: Chem. & Met. Eng., 28, 805 (1923).

[118] Miller: Alexander's "Colloid Chemistry," 3, 119 (1931); cf. Trans. Am. Inst. Chem. Engrs., 15 I, 241 (1923); Oil & Gas J., 23, 104, 151, 158 (1924).

[119] Cf. Fulreader: Ind. Eng. Chem., 21, 691 (1929).

[120] Cf. Waterman and van Tussenbroek: Brennstoff-Chem., 8, 20 (1927); 9, 37, 397 (1928).

Since the adsorption process removes sulfur compounds without taking out the unsaturated hydrocarbons, it was possible to demonstrate that the former are responsible for most of the soot and smoke sometimes obtained in a kerosene flame. Gasoline purified by silica gel is said to give less carbon than ordinary gasoline; and the same is true for motor benzol.[121] Moreover, certain gel-refined lubricating oils are reported to give only about one-half as much carbon as the best ordinary oils, and about one-fifth as much as the poor grades, when used with the best grade of gasoline.

Silica gel may be used to adsorb from natural gas the low-boiling gasoline vapors[122] which are subsequently recovered and blended with refinery gasoline to increase the volatility of the latter. It may be employed also for estimating the easily condensable hydrocarbons in natural gas and coal gas. For these purposes, activated carbon appears to be the more satisfactory adsorbent.[123] Furness[124] and Williams[125] claim that silica gel is superior both to activated carbon and to oil absorbents for the recovery of benzol and motor spirit from coke-oven gas;[126] but this is disputed by Urbain,[127] who reports that charcoal has great superiority over silica gels as a selective adsorbent of hydrocarbon vapors, especially if they are considerably diluted, as they usually are.

Probably the most important technical application of silica gel is as a carrier for platinum in the contact sulfuric acid process.[128]

Adsorption by silica gel is suggested as a method for recovering the oxides of nitrogen in the arc process for the fixation of nitrogen.[129] The removal is complete from rapid air currents at low concentration, and by heating the gel, the adsorbed oxides may be recovered ready

[121] Fieldner and Jones: Bur. Mines, Serial 2517 (1923); Chem. & Met. Eng., 29, 543 (1923).

[122] Burrell: Chem. & Met. Eng. 29, 544 (1923).

[123] Kroch: Petroleum Z., 20, 732; cf., however, Singer: 279 (1924); Green and Maw: Colliery Guardian, 128, 88 (1924).

[124] Chemistry & Industry, 42, 850 (1923).

[125] J. Soc. Chem. Ind., 43, 97T (1924).

[126] Lummus: U. S. Pat. 1,336,360 (1920).

[127] Gas. J., 167, 449 (1924); cf. Chaney, Ray, and St. John: Ind. Eng. Chem., 15, 1244 (1923); Hoffert: Gas. J., 170, 654 (1925).

[128] Patrick: U. S. Pat. 1,297,724 (1919); Latshaw and Reyerson: J. Am. Chem. Soc., 47, 610 (1925); Morris and Reyerson: J. Phys. Chem., 31, 1332; Reyerson and Swearingen: 88 (1927); 32, 113 (1928); Holmes, Ramsay, and Elder: Ind. Eng. Chem., 21, 850 (1929); Miller: Alexander's "Colloid Chemistry," 3, 119 (1931).

[129] Daniels and McCollum: Ind. Eng. Chem., 15, 1173 (1923); Almquist, Gaddy, and Braham: 17, 599 (1925).

for liquefaction or for absorption in water to give concentrated nitric acid.

Nutting[130] estimates the maximum adsorptive force of silica for water to be equivalent to 17,000 atmospheres. It is therefore a good drying agent and may be employed in drying air for blast furnaces[131] and to take up water vapor from the rapid vaporization of the liquid in the vacuum refrigeration process.[132] It is also suggested for use as a powder to adsorb perspiration. For this purpose it serves the double function of taking up the moisture and of adsorbing the odorous substances given out by the pores of the body while performing their natural functions.[132]

As a filtering agent, a refined silica known as "Filtrol" is said to be three times as good a decolorizer for vegetable oils as is the standard fuller's earth, and to be effective at a lower temperature. Besides its decolorizing property, the silica adsorbs water, free sulfuric acid, sulfur compounds, and colloidal particles.[133] The gel is also recommended for filtering pharmaceutical preparations,[134] since it gives more efficient results than an equal amount of talc, the filtering agent usually employed. Although silica gel is a good adsorbent for various gases, it is not, in general, a good catalyzer.[135] In the esterification of acetic acid with alcohol, however, it has been found to be twice as active as titania, the best catalyst previously known for this reaction. It is also an efficient catalyst for the alkylation of aniline,[136] but its effectiveness falls off rapidly in the first hour or so owing to the formation of aldehydes which react with aniline to give easily polymerized bodies.

Summarizing the commercial uses of the gel, Miller[118] says: "These applications include the purification of light oil for the production of motor benzol, refining of petroleum distillates, dehydration and purification of carbon dioxide, hydrogen, oxygen, nitrogen, helium, recovery and dehydration of chlorine, air conditioning systems, drying blast for blast furnaces and cupolas, refrigeration for transportation of perishable products, and general domestic uses including dairies, cosmetic, and medicinal uses."

[130] J. Phys. Chem., **31**, 531 (1927).

[131] Krull: Z. Ver. deut. Ing., **70**, 907 (1926); Kroupa: Montan. Rundschau, **21**, 434 (1929); Lewis: Engineering, **124**, 853 (1927); Iron & Coal Trades Rev., **65**, 444 (1927).

[132] Fulton: Chem. Age, **31**, 521 (1923).

[133] Kelly: Cotton Oil Press, **7**, 38 (1923).

[134] Krantz: J. Am. Pharm. Assoc., **11**, 701 (1922).

[135] Milligan and Reid: Science, **53**, 576 (1921).

[136] Brown and Reid: J. Am. Chem. Soc., **46**, 1836 (1924).

SILICA AEROGEL

It is a well-known fact that removal of all the water from silica gel by heating causes it to lose most of its adsorbing power as a result of coalescence of particles and the consequent decrease in porosity. Kistler[137] has demonstrated, however, that it is possible to replace the liquid in a gel by a gas with little or no shrinkage. The method consists in displacing the liquids successively by liquids that are completely miscible with the preceding and succeeding one (e.g., water, alcohol or water, alcohol, ether) the last one having a low critical temperature. The resulting jelly is then placed in an autoclave with an excess of liquid and heated above the critical point. On allowing the gas to escape, a coherent expanded aerogel is obtained. A silica aerogel having an apparent density of 0.02 was prepared in this way as a slightly opalescent but quite transparent glassy solid. The method is general, and aerogels have been made of silica, alumina, tungstic, ferric, and stannic oxides, nickel tartrate, cellulose, nitrocellulose, gelatin, agar, and egg albumin.

SILICA SOL

FORMATION

More than a century and a half ago Pott[138] reported the preparation of a "semisolution" of silica, but Graham is usually credited with the discovery of silica sol. Graham[139] added 2/3 the amount of water glass necessary for immediate gelatinization to 10% HCl, and dialyzed the resulting mixture. Starting with highly purified chemicals, Jordis[140] obtained a pure sol containing 1.5% SiO_2 by 6 weeks' dialysis. Further purification in a special apparatus[141] finally led to the separation of plates of silica from a sol containing 0.6% SiO_2. If sulfuric acid instead of hydrochloric is used in preparing the sol, it is impossible to remove all the sulfate by dialysis. A sol containing 2 to 3 mols of sodium sulfate per mol of silica can be concentrated by evaporation until the silica content is 6 to 12% of the entire mass.[142]

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[137] Nature, **127**, 741 (1931); J. Phys. Chem., **36**, 52 (1932).
[138] See Walden: Kolloid-Z., **9**, 145 (1911).
[139] Phil. Trans., **151**, 183 (1861).
[140] Z. anorg. Chem., **34**, 455; **35**, 16 (1903); **44**, 200 (1905); Z. Elektrochem., **11**, 835 (1905).
[141] Jordis: Z. Elektrochem., **8**, 677 (1902).
[142] Zsigmondy and Heyer: Z. anorg. Chem., **68**, 169 (1910).

Schwarz[143] peptized a fresh silica gel with ammonia and removed the excess peptizing agent in a vacuum desiccator over sulfuric acid; and Khalizev,[144] prepared highly concentrated stable sols with potassium hydroxide as the peptizing agent, removing the excess with tartaric acid.   Sols are also obtained by hydrolysis of methyl silicate[145] and of silicon sulfide, chloride, and fluoride.[146]   It is formed also by electrolyzing a solution of sodium silicate with a mercury cathode.[147] Lottermoser and Kiehn[148] investigated the purification by dialysis of sols prepared in various ways.   It was found impossible to prepare electrolyte-free sols, but the purest preparations resulted from electrodialysis of the sol formed by hydrolysis of silicon tetrachloride using clay at the cathode and collodion at the anode as the dialyzing membranes.

All the above procedures give sols similar to those formed by Graham's method.   Bradfield[149] obtained a sol with somewhat different properties by washing gelatinous silica with the supercentrifuge until it was practically free from electrolyte.   If the washing is repeated a sufficient number of times, the hydrogen ion concentration of the sol becomes constant at $pH = 6.5$, whether approached from the acid or alkaline side.   Hardy[150] attributes this slight acidity to the ability of certain of the adsorbed water molecules to ionize.   The highly purified sol can be concentrated on the water bath to a syrupy consistency which can be brought back to the original sol condition by adding water.   If the boiling is carried too far, minute crystals of hydrous silica separate from the sol.[151]   Even the most concentrated sols show no tendency to gel, probably because the secondary aggregates have been broken up by repeated centrifuging and repeptization, leaving small groups of primary particles that entangle relatively little water.

Lenher[26] prepared silica sol by grinding Ottawa sand for several

[143] Schwarz: Kolloid-Z., **28**, 77 (1921); **34**, 23 (1924); Schwarz and Stöwener: Kolloid-Beihefte, **19**, 171 (1924); Grundmann: **18**, 197 (1923).

[144] J. Russ. Phys.-Chem. Soc., **61**, 1233 (1929).

[145] Grimaux: Compt. rend., **98**, 1434 (1884).

[146] Ebler and Fellner: Ber., **44**, 1915 (1911).

[147] Treadwell and Wieland: Helv. Chim. Acta, **13**, 842 (1930).

[148] Kolloid-Beihefte, **35**, 123 (1932); cf. Oka: Chem. News, **138**, 67 (1929); J. Soc. Chem. Ind., Japan, **31**, 1281, 1289 (1929).

[149] J. Am. Chem. Soc., **44**, 965 (1922).

[150] J. Phys. Chem., **30**, 262 (1926).

[151] Cf. Bachmann: Z. anorg. Chem., **100**, 1 (1917); Zsigmondy-Spear: "Chemistry of Colloids," 137 (1917); Schwarz and Stöwener: Kolloid-Beihefte, **19**, 171 (1924).

days until the particles were less than 0.004 mm in diameter. When such finely divided silica is heated with an excess of water in a pressure bomb at 300–450°, gels are formed containing 15 to 18% water. Ray[152] claims that crystalline quartz is partly converted into amorphous silica by prolonged grinding, but the claim appears to be without experimental foundation.[153]

An alcosol of silica may be prepared by hydrolyzing ethyl silicate in absolute alcohol with the calculated amount of water containing a small amount of acid.[154] The acid may be removed by adding a metallic oxide like silver oxide which forms a salt insoluble in alcohol, or by electrodialysis.

CONSTITUTION

Mylius and Groschuff[155] believe that, at the moment of its formation from water glass, silicic acid exists as such in molecular solution which passes unchanged through a dialyzing membrane, and that the colloidal state results from polymerization of the acid with the splitting off of water. Willstätter, Kraut, and Lobinger[156] likewise claim to get silicic acids in molecular solution by adding the calculated amount of silver oxide paste to a solution of silicon tetrachloride. From measurements of the freezing-point lowering of the resulting solution and correcting for the part due to hydrochloric acid, a molecular weight of approximately 60 corresponding to H_2SiO_3 was obtained.[157] Willstätter deduced that the above acid can exist only in 0.002 to 0.001 N HCl, but Gruner and Elöd[157] claimed to get it in 0.014 N HCl. The compound is very instable and undergoes condensation rather rapidly with the formation of colloidal silica. Thus H. and W. Brintzinger[158] saponified tetraethyl orthosilicate with 0.002 N HCl and measured the change in molecular weight as calculated from lowering of the freezing point. It rose from 153 at the start to 290 after 2 days, 550 after 3 days, 862 after 4 days, and 8260 after 45 days. Altogether irrespective of whether the freezing-point data are accurate or applicable after the silica has become colloidal, it

[152] Proc. Roy. Soc. (London) 101A, 509 (1922).
[153] Sosman and Merwin: J. Wash. Acad. Sci., 14, 117 (1924).
[154] Inaba: Bull. Inst. Phys. Chem. Research (Tokyo) 7, 948; English Ed., 1, 92 (1928).
[155] Ber., 39, 116 (1906).
[156] Ber., 58B, 2462 (1925); 61B, 2280 (1928); 62B, 2027 (1929); 64B, 1709 (1931).
[157] Gruner and Elöd: Z. anorg. Chem., 208, 317 (1932).
[158] Z. anorg. Chem., 196, 44 (1931); cf. Treadwell and König: Helv. Chim. Acta, 16, 468 (1933).

is apparent that the acid first formed polymerizes rapidly, forming larger aggregates,[159] the process being continued and approaching crystalline silica as a limit.   Some believe that the intermediate products between H_2SiO_3 and SiO_2 consist of an indefinite number of definite condensed silicic acids, but there is no proof of this.   The evidence indicates that the gel thrown down from alkali silicates with acid is hydrous cristobalite, and it is reasonable to suppose that the sol aged for a few days is essentially hydrous cristobalite.

Pauli and Valko[160] formulate the constitution of the sol $[x(SiO_2)nH_2O]ySiO_3H^+ + yNa^+$ or yH^+, since the Na^+ ions can be replaced by H^+ ions in the Graham sol.   Sols highly purified by electrodialysis have a pH value as low as 3.23;[161] by ordinary dialysis the pH value is between 4.5 and 6.3.

PROPERTIES AND USES

Well-purified silica sols are quite clear, colorless liquids exhibiting but little inhomogeneity in the ultramicroscope and giving only a very slight depression of the freezing point.   As ordinarily prepared, the sols are negatively charged, but this negative charge may be decreased continuously by the addition of hydrochloric acid, becoming zero and finally positive without precipitation taking place.[162]   Unlike ferric oxide sol, silica sol containing a little chloride becomes turbid on adding silver nitrate.

Unlike the sols of the hydrous oxides previously considered, silica sol is relatively insensitive to the action of electrolytes.   Thus Laskin[163] showed that coagulation is effected only by relatively high concentrations of such materials as the chlorides and nitrates of calcium, barium, lithium, aluminum, lanthanum, thorium, and iron. The principal factor in the coagulation appears to be the dehydrating action on the colloidal particle of highly hydrated ions—a salting-out effect.   Silica sol is therefore quite hydrophilic, exhibiting a strong analogy to protein sols of the type of albumin.[164]   However, its behavior is quite different from albumin in one respect, the viscosity. With protein sols the viscosity is determined by the charge, but the

[159] Cf. Vail: J. Soc. Chem. Ind., **44**, 214T (1925).

[160] Kolloid-Z. (Zsigmondy Festschrift) **36**, 334 (1925); **38**, 289 (1926).

[161] Rabinovich and Laskin: Z. physik. Chem., A134,387 (1928); Laskin: Kolloid-Z., **45**, 129 (1928); Treadwell and König: Helv. Chim. Acta, **16**, 468 (1933).

[162] Lösenbeck: Kolloid-Beihefte, **16**, 27 (1922); cf. Grundmann: **18**, 197 (1923).

[163] Kolloid-Z., **45**, 129 (1928); cf. Postma: Rec. trav. chim., **51**, 726 (1932).

[164] Pauli-Valko: "Elektrochemie der Kolloide," 513 (1929).

relationship between viscosity and charge in silica sols appears to be much more complicated.[165]

Freundlich and Cohn[166] showed that a very small amount of alkali sensitizes the negative silica sol toward sodium chloride, whereas larger amounts stabilize it. The stabilization is probably due to the solvent action of the alkali which decreases the size of the particles and lowers the concentration of the sol. The cause of the sensitization by small amounts of hydroxyl ion is not obvious. Freundlich[167] attributes this effect also to chemical action, but it is difficult to see why chemical action of alkali on the particles should first sensitize and then stabilize the sol. The whole phenomenon should be reinvestigated.

The adsorption of ions from hydrochloric acid by the particles of colloidal silica has been measured by application of Donnan's theory of membrane equilibrium[168] (Vol. I, p. 315).

Silica is present to a certain extent in the sol form in commercial "silicate of soda" and, as such, has wide applications. These will be taken up under colloidal silicates in a volume dealing with colloidal salts. In the pure state, silica sol is of little or no technical importance. It has been recommended in the treatment of pulmonary tuberculosis; but it is of questionable value.[169] It is administered along with protein in the form of tablets or better by subcutaneous or intramuscular injection.[170] Great care must be taken not only in the preparation of the sol but also in its administration.[171]

Kramer[172] finds that the addition of animal or vegetable oils to a 0.2% solution of sodium silicate gives a fine, stable emulsion in which many of the drops exhibit Brownian movement. The fatty acid of the oil combines with the alkali to form soap, liberating colloidal silica which acts as a protecting colloid for the emulsion. The careful addition of dilute hydrochloric acid produces a silica gel emulsion, whereas the addition of lime water causes coagulation, forming a

[165] Kruyt and Postma: Rec. trav. chim., 44, 765 (1925).

[166] Kolloid-Z., 39, 28 (1926).

[167] "Kapillarchemie," 3rd ed., 2, 400 (1932).

[168] Ganguly and Krishnamurti: Trans. Faraday Soc., 24, 401 (1928).

[169] Kadisch: Beitr. Klin. Tuberk., 53, 111 (1922); Susanna: Physiol. Abstracts, 11, 589 (1926).

[170] Kühn: Münch. med. Wochschr., 67, 253 (1920); Z. Tuberk., 32, 320 (1920); Kahle: Beitr. Klin. Tuberk., 47, 296 (1921); Gonnermann: Z. physiol. Chem., 99, 255 (1917).

[171] Gye and Purdy: Brit. J. Exptl. Path., 3, 75, 86 (1922).

[172] Kolloid-Z., 31, 149 (1922).

cheese-like coagulum and a thin liquid. These experiments are said to reproduce synthetically the changes in the tissue which take place in tuberculosis: Alkali silicates form a fat emulsion in the tissues. The hydrous silica in the emulsion has a strong affinity for lime which is withdrawn from the blood and causes the caseation of the emulsified fat, as in the experiments referred to above. Carbonic acid then acts slowly on the "silica cheese," converting the lime into carbonate, a process designated by the pathologists as calcification. There remains in the tissues the small amount of hydrous silica which served originally as the protecting colloid for the emulsion. In line with this, Neyland found, in tubercular lymph glands of oxen, a silica content of 0.27 g SiO_2 per kg of dry tissue, whereas a calcified lymph gland contained 1.54 g SiO_2 per kg of tissue.[173]

THE HYDROUS OXIDES OF GERMANIUM

Hydrous Germanium Dioxide

The Gel. Germanium dioxide is precipitated in a gelatinous form by the hydrolysis of germanium tetrachloride[174] or tetrabromide[175] or by passing carbon dioxide into a solution of alkali germanate.[176] It forms no hydrates,[177] but it holds to the last trace of adsorbed water quite strongly, complete dehydration requiring a temperature of 950°.[178] The precipitated oxide is fairly soluble, giving an acid solution,[179] from which microscopic rhombic crystals separate on evaporation. X-ray analysis of the hydrous oxide shows that the crystals belong to the "cristobalite" type.[180] Similar crystals are obtained by the devitrification of the glass obtained when the fused dioxide solidifies.[181]

By igniting the "soluble" hexagonal oxide at a temperature of

[173] Kahle: Beitr. Klin. Tuberk., **47**, 316 (1921).

[174] Winkler: J. prakt. Chem. (2) **34**, 211 (1886); Dennis and Johnson: J. Am. Chem. Soc., **45**, 1380 (1923).

[175] Dennis and Hance: J. Am. Chem. Soc., **44**, 299 (1922).

[176] Winkler: J. prakt. Chem. (2) **34**, 177 (1886).

[177] Van Bemmelen: Rec. trav. chim., **6**, 205 (1887); Schwarz, Schenk, and Giese: Ber., **64B**, 362 (1931).

[178] Dennis, Tressler, and Hance: J. Am. Chem. Soc., **45**, 2033 (1923).

[179] Winkler: J. prakt. Chem. (2) **34**, 211 (1886); Müller and Iszard: Am. J. Med. Sci., **163**, 364 (1922); Pugh: J. Chem. Soc., 1537 (1929); Guleziau and Müller: J. Am. Chem. Soc., **54**, 3151 (1932).

[180] Müller: Proc. Am. Phil. Soc., **65**, 193 (1926).

[181] Zachariasen: Z. Krist., **67**, 226 (1928).

about 380°, Müller and Blank[182] prepared an "insoluble" oxide which possesses entirely different properties and is tetragonal in crystal structure, giving an x-ray diffraction pattern of the "rutile" type.[183] A more complete conversion is attained by heating the ordinary oxide to 350° in a bomb tube.   Laubengayer and Morton[184] made a detailed study of the properties of the two oxides and of the phase relations in the one component system.   The evidence is against the existence of a third modification of the oxide.

The Sol. Hydrous germanium dioxide is peptized by washing, giving a negatively charged hydrosol[185] which is not very stable because of the solvent action of the water.   For the same reason, hydrogels of germania comparable with those of silica are not formed. However, Laubengayer and Brandt[186] obtained a jelly by hydrolysis of an alcoholic solution of germanium tetraethoxyl by water.   Germania gel, formed by drying the jelly and igniting to a temperature of 180°, has an adsorptive capacity greater than Patrick's silica gel for such vapors as benzene, carbon tetrachloride, and ether.

The action of alkalis on hydrous germanium dioxide gives partly alkali germanate and partly a colloidal dispersion of the oxide.[187]

Colloidal germanium dioxide is claimed by some to have therapeutic value in the treatment of secondary and pernicious anemia,[188] but this is questioned by others.[189]

Hydrous Germanous Oxide

Unlike silicon, but like tin, germanium forms an "ous" oxide. This is precipitated in a gelatinous form by the action of alkalis on a solution of $GeCl_2$ or by the hydrolysis of germanium chloroform, $GeHCl_3$.   Dennis and Hulse[190] prepared the hydrous germanous

[182] J. Am. Chem. Soc., **46**, 2358 (1924); Müller: Proc. Am. Phil. Soc., **65**, 193 (1926).

[183] Goldschmidt: Naturwissenschaften, **14**, 295 (1926); Z. physik. Chem., **B17**, 172 (1932).

[184] J. Am. Chem. Soc., **54**, 2303 (1932).

[185] Roth and Schwartz: Ber., **59B**, 338 (1926).

[186] J. Am. Chem. Soc., **54**, 549 (1932).

[187] Pugh: J. Chem. Soc., 1537 (1929).

[188] Lenker: Penn. Med. J., **26**, 86 (1922); Kast, Croll, and Schmitz: J. Lab. Clin. Med., **7**, 643 (1922); Müller and Iszard: Am. J. Med. Sci., **163**, 364 (1922); J. Metabolic Research, **3**, 181 (1923).

[189] Minot and Sampson: Boston Med. Surg. J., **189**, 629 (1923); Hueper: Am. J. Med. Sci., **181**, 820 (1931).

[190] J. Am. Chem. Soc., **52**, 3553 (1930); *cf.* Bardet and Tchakirian: Compt. rend., **186**, 637 (1928).

oxide free from germanic oxide by reducing germanic chloride with hypophosphorus acid out of contact with air, and precipitating with dilute ammonia.   The freshly formed gel varies in color from yellow to red, depending on the conditions of precipitation.   It is probable that the yellow preparation is the more hydrous since dehydration causes a change in color from red to brown to black.   The loss of water is continuous, giving no indication of a definite hydrate.

The yellow hydrous oxide is peptized by boiling water, giving a red sol.   According to Hantzsch,[191] it is very slightly soluble in water, acting as a weak monobasic acid of the constitution $HGeO \cdot OH$ analogous to formic acid.   The hydrous oxide is almost insoluble in alkalis, but it is peptized by them, giving red colloidal solutions.

[191] Z. anorg. Chem., **30**, 289 (1902).

CHAPTER VIII

THE HYDROUS OXIDES OF TIN AND LEAD

HYDROUS STANNIC OXIDE

As early as 1812, Berzelius[1] called attention to differences between the hydrous oxide formed by precipitation of stannic chloride with alkali and the product resulting from the action of nitric acid on tin. Berzelius thought at first that he was dealing with two degrees of oxidation; but this was disproved by subsequent investigations of Davy, Gay-Lussac, and Berzelius himself. Thus, Berzelius was led to conclude that the two preparations, having widely different properties, were simply modifications of the same oxide. This was the first recognized example of isomerism, a term suggested by Berzelius[2] a little more than a century ago.

PRECIPITATED STANNIC OXIDE

Since the oxides formed by precipitation of stannic salts and by the action of nitric acid on tin both give a very slight acid reaction when shaken with water, they are commonly designated as ortho-stannic and metastannic acids, respectively. The earlier chemists regarded them as distinct chemical individuals and recognized the similarities and differences between the two that are listed in Table XVIII. In the light of what is now known of the colloidal state of matter, the statements of earlier chemists concerning the properties of these bodies are inaccurate in many respects. Since the different substances are more properly termed hydrous oxides than acids, the so-called orthostannic acid will be referred to as the freshly formed or α-oxide and the metastannic acid as the aged or β-oxide.

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[1] *Cf.* "Lehrbuch," 1st ed., **2**, 271 (1826).
[2] Pogg. Ann., **19**, 305 (1830).

TABLE XVIII

Distinctions Commonly Made between the So-called Ortho- and Metastannic Acids

	Orthostannic acid	Metastannic acid
Preparation......	Precipitation from solution of stannic salt	Action of concentrated HNO_3 on tin
Formula.........	H_2SnO_3	H_2SnO_3
Action of HNO_3..	Easily soluble	Insoluble
Action of HCl....	Easily soluble; not precipitated by excess acid	Insoluble. Product treated with concentrated acid and filtered dissolves in water but precipitates again with excess acid
Action of H_2SO_4 .	Easily soluble	Insoluble but swells in concentrated acid forming a mass that is soluble in water
Action of caustic.	Easily soluble; not precipitated by excess alkali	Soluble when freshly prepared; precipitated by excess alkali
Action of $SnCl_2$ ..	No action	Yellow precipitate from solution in HCl

FORMATION

The typical α-oxide is prepared by precipitation of stannic chloride or stannic bromide with alkali[3] or with an excess of the carbonate of barium or calcium;[4] and by precipitating a solution of soluble crystalline stannate having the formula $M_2Sn(OH)_6$[5] with mineral acid.[6] Rose[7] claimed to get the α-oxide by hydrolysis of a dilute solution of stannic chloride at the boiling point. This is unquestionably incorrect, since it has been observed repeatedly that α-oxide, formed by hydrolysis of stannic chloride at low temperatures, goes over to β-oxide gradually on standing or very rapidly at the boiling point.[8] Similar observations have been made with stannic bromide[9] and with stannic nitrate. Lorenz[10] obtained the α-oxide by electrolyzing an

[3] Berzelius: "Lehrbuch," 5th ed., 2, 596 (1848).

[4] Schiff: Ann., 120, 47 (1861).

[5] Bellucci and Parravano: Z. anorg. Chem., 45, 142 (1905).

[6] Fremy: Ann. chim. phys. (3) 12, 463 (1844); 23, 385 (1848); Kühl: Pharm. Ztg., 53, 49 (1908).

[7] Pogg. Ann., 75, 1 (1848).

[8] Barfoed: J. prakt. Chem., 101, 368 (1867); Engel: Compt. rend., 124, 765; 125, 464, 651, 709 (1897); Zsigmondy: Ann., 301, 368 (1898).

[9] Lorenz: Z. anorg. Chem., 9, 371 (1895).

[10] Z. anorg. Chem., 12, 436 (1896).

alkali chloride, nitrate, or sulfate solution using a platinum cathode and a tin anode.

The typical β-oxide is prepared by the oxidation of tin with moderately concentrated nitric acid. Weber[11] claimed that acid of 1.2 sp. gr. gave both α- and β-oxides, whereas acid of 1.35 sp. gr. produced a clear solution from which β-oxide was obtained by warming. Hay[12] and Scott[13] likewise observed the complete dissolution of tin in moderately dilute nitric acid (1 : 1) at 2°, from which β-oxide precipitated by warming or by standing at ordinary temperatures. The solution contained stannous nitrate, stannic nitrate,[14] and doubtless colloidal stannic oxide[15] in varying amounts, depending on the concentration of acid and the temperature. As before noted, β-oxide is produced whenever a dilute solution of a crystalline tin salt undergoes hydrolysis at the boiling temperature. A solution of amorphous sodium metastannate, so called, likewise precipitates β-oxide when heated.

From this survey, it is evident that either oxide may be prepared by hydrolysis of stannic salts under suitable conditions. In all probability the first product of this hydrolysis is always α-oxide, which subsequently goes over to β-oxide quite slowly at ordinary temperatures but with increasing rapidity as the temperature is raised.

COMPOSITION

By drying different precipitated oxides under suitable conditions, early investigators have reported the preparation of a variety of supposedly definite oxide hydrates, and hydrated acids of tin.[16] Extended investigations of van Bemmelen, on the change in vapor pressure of different preparations with the temperature, indicated that such compositions were purely accidental, depending on the method of formation, the method of drying, the temperature, and the age of the sample. Van Bemmelen's observations were confirmed and extended and his conclusions reaffirmed by Lorenz,[17] Mecklenburg,[18] and

[11] Pogg. Ann., **122**, 358 (1864).

[12] Chem. News, **22**, 298 (1870).

[13] Chem. News, **22**, 322 (1870).

[14] Walker: J. Chem. Soc., **63**, 845 (1893).

[15] Mecklenburg: Z. anorg. Chem., **64**, 370 (1909).

[16] Fremy: Ann. chim. phys. (3) **12**, 463 (1844); **23**, 393 (1848); cf. Weber: Pogg. Ann., **122**, 358 (1864); Graham: Ann., **13**, 141 (1835); Schaffner: **51**, 168 (1844)· Carnelley and Walker: J. Chem. Soc., **53**, 83 (1888).

[17] Z. anorg. Chem., **9**, 369 (1895).

[18] Z. anorg. Chem., **64**, 368 (1909); **74**, 207 (1912); **84**, 121 (1913).

Weiser.[19]   In recent years, however, Willstätter and his collaborators[20] adopted the older view that the behavior of the variety of oxides could be explained best by assuming the existence of more or less stable hydrates.   Willstätter claimed to remove all the adsorbed water from a compound by drying rapidly in vacuum or by leaching with acetone.   The composition of a gel formed in a special way, and dried by the acetone method at -35 to $+10°$, was represented by the formula $Sn(OH)_4 \cdot H_2O$; but when dried at room temperature the analysis showed a composition $Sn(OH)_4$, which was regarded as the first member of a series of α-stannic acids.   In an aqueous medium, $Sn(OH)_4$ was supposed to go over into other less basic members of the series.   Thus by suitable conditions of precipitation and drying with acetone at 0 to $10°$, orthodistannic acid was supposedly formed; at 35 to $46°$, orthotristannic acid; and so on.   Different so-called β-stannic acids were likewise prepared and many of them assigned formulas.

As proof of hydrate formation, Willstätter cites the regions of almost constant water content in the temperature-composition curves of acetone-dried preparations.   Such evidence is altogether inconclusive, particularly when the nature and location of the "flats" in the curves are determined almost exclusively by the history of the sample.   The same may be said of the "flats" in the temperature-vapor pressure curves of van Bemmelen.   The adsorptive capacity of a hydrous oxide for water at different stages of dehydration is determined by the physical character of the preparation; hence a "flat" corresponding to a definite hydrate is purely accidental and can be duplicated only by following a set method of procedure in precipitation, aging, and drying.   Willstätter's comparison of the behavior of hypothetical, high-molecular, hydrated, stannic acids with their groups Sn : O and Sn·OH, to that of carbohydrates with their groups C : O and C·OH, appears highly fantastic and illusionary.   As Posnjak[21] points out: "Willstätter and his collaborators did not bring forth a single new fact, but rather take the problem back some fifty years and only add to the confusion."

Fortunately, Posnjak was able to settle the question of the composition of the so-called α- and β-stannic acids by the aid of x-ray

[19] J. Phys. Chem., 26, 654 (1922).

[20] Willstätter, Kraut, and Fremery: Ber., 57B, 63, 1491 (1924); Willstätter and Kraut: Ber., 59B, 2541 (1926); Kolloid-Z., 49, 353 (1929); cf., also, Sisley and Meunier: Bull. soc. chim. (4) 51, 939 (1932); Simon and Rath: Z. anorg. Chem., 202, 200 (1930).

[21] J. Phys. Chem., 30, 1073 (1926); Yamada: J. Chem. Soc. Japan, 44, 210 (1923).

diffraction analysis. Samples of the so-called α- and β-oxides were found to give identical diffraction patterns which in turn were identical with that of the mineral cassiterite—anhydrous stannic oxide. This result has been confirmed by Förster[22] and by Hüttig and Döbling,[23] so that we are certain of the facts. The α- and β-stannic oxides are not isomers but are structurally the same: stannic oxide with more or less adsorbed water. The differences in properties are due to the size and extent of coalescence of the primary particles into secondary aggregates. Similar conclusions were reached by Pascal[24] from measurements of the molecular susceptibilities of various preparations.
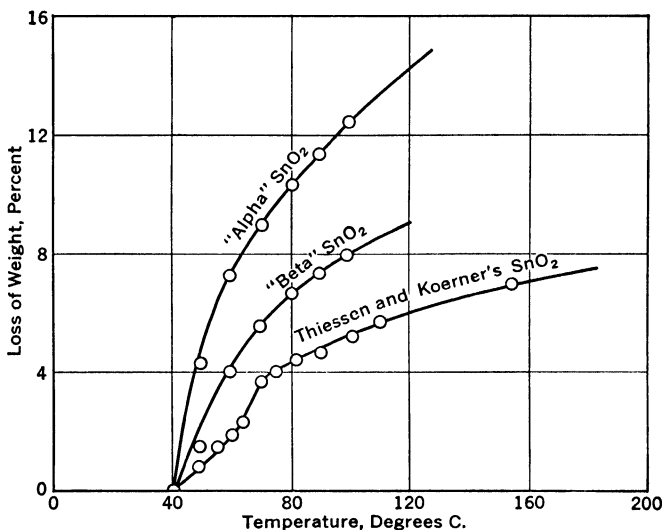
Fig. 41.—Thermal dehydration of stannic oxides.

In spite of the conclusive nature of the evidence against the existence of isomeric forms and hydrates of stannic oxide, Thiessen and Koerner[25] claim that a stannic oxide gel prepared by the slow hydrolysis of an alcoholic solution of stannic ethylate gives pressure-temperature and composition-temperature curves that indicate the formation of no less than 6 definite hydrates. This could not be confirmed in the author's laboratory[26] as shown by the dehydration isobar given in

[22] Physik. Z., **28,** 151 (1927); Havestadt and Fricke: Z. anorg. Chem., **188,** 357 (1930).

[23] Ber., **60B,** 1029 (1927); Gutbier, Hüttig, and Döbling: **59B,** 1232 (1926).

[24] Compt. rend., **175,** 1063 (1922).

[25] Z. anorg. Chem., **195,** 83 (1931).

[26] Weiser and Milligan: J. Phys. Chem., **36,** 3030 (1932).

Fig. 41, together with similar isobars for typical α- and β-oxides. In every case, smooth curves were obtained indicating the absence of hydrates. The change in direction at a temperature of 60–70° with the oxide made by Thiessen and Koerner's method is not due to a hydrate but to the presence of a small amount of alcohol in the sample. The breaks in the curves of Thiessen and Koerner were the result of faulty technique, possibly the failure to allow sufficient time for equilibrium to be established under a given set of conditions. Finally, x-ray diffraction patterns, obtained by dehydrating Thiessen and Koerner's gel at definite temperatures, show that no definite hydrates are actually formed, the several alleged hydrates consisting of stannic oxide (cassiterite) of varying particle size with varying amounts of adsorbed water.

PROPERTIES OF STANNIC OXIDE GEL

The gradual change in the composition of hydrous stannic oxide is accompanied by marked changes in the physical constants of the gel. Thus Hüttig[27] finds a relationship between the specific heat and the age and water content of the gel which may be expressed by the following equation: $\log \dfrac{C_0}{C} = \dfrac{k}{N}$, where C_0 is the molecular heat of pure water, C is the molecular heat of the hydrous oxide with N mols of water to one mol of oxide, and k is a constant. A similar relationship holds between the vapor pressure and water content. Havestadt and Fricke[28] observed a slow decrease in the dielectric constant of the oxide with time. The action of electrolytes on fresh and aged preparations will be considered in the following sections.

Action of Acids

Hydrochloric Acid. The freshly prepared oxide is readily soluble in dilute hydrochloric acid and is not precipitated by an excess of acid even at the boiling point, whereas the aged oxide is insoluble in both dilute and concentrated acid. However, if the aged oxide is treated with concentrated hydrochloric acid, a gelatinous mass is formed which Engel[29] believes to be a salt, metastanyl chloride. This product is taken up by water but is reprecipitated by boiling or by adding concentrated hydrochloric acid. In view of the variety

[27] Hüttig, Magierkiewicz, and Fichmann: Z. physik. Chem., **A141**, 1 (1929).
[28] Z. anorg. Chem., **188**, 357 (1930).
[29] Compt. rend., **124**, 765; **125**, 464, 651, 709 (1897).

of acids that are supposed to be derived from stannic oxide, it is not surprising to encounter a number of basic salts of tin. Thus Engel claims to get $SnCl_4$, $Sn_5O_8Cl_2 \cdot 4H_2O$, and $Sn_5O_9Cl_2 \cdot 2H_2O$, corresponding to his ortho, meta, and para acids.[30] Although $SnCl_4$ is obtained by the action of concentrated HCl on the α-oxide,[31] and H_2SnCl_6[32] is formed by passing gaseous HCl into a solution of $SnCl_4$, there is little or no evidence to support the view that the amorphous precipitates obtained from solutions of α- and β-oxide, under varying conditions, are definite compounds. Van Bemmelen[33] was the first to recognize the real nature of such solutions. He proved it to be incorrect to speak of "solubility" of the oxides in acid by showing that the acid which holds the α-oxide in what was thought to be a true solution may be neutralized almost entirely without the oxide precipitating; that the salt formed may be removed by dialysis without precipitation taking place; and finally, that the solutions may be boiled, converting α- into β-oxide which likewise does not precipitate unless the boiling is continued too long.[34] Van Bemmelen also observed the adsorption of HCl by both oxides. Below the concentration which causes peptization, the adsorption isotherms have the usual form, indicating that the amount adsorbed depends on the concentration of acid in contact with the oxide. The adsorption was found to be less with β-oxide than with α-oxide, and the older and denser the β-oxide, the less was the adsorption.

The action of HCl on the different oxides can now be explained. The newly formed oxide possesses a softer and looser structure than the aged oxide, and so the former is readily peptized by dilute acid and the sol is stable even in the presence of a very small amount of acid. A high concentration of acid converts it into a true solution of $SnCl_4$. The coarser, denser particles of the aged oxide are insoluble and are not peptized by dilute HCl. Concentrated acid, on the other hand, peptizes the oxide, and if the excess of acid is poured off, the particles will go into solution in water (dilute HCl) from which they are precipitated by excess acid or by boiling. Since α-oxide changes to β-oxide even at ordinary temperatures and in contact with water,

[30] Cf. Tschermak: J. prakt. Chem., **86**, 334 (1862); Mallet: J. Chem. Soc., **35**, 524 (1879); Scheurer-Kestner: Ann. chim. phys. (3) **58**, 471 (1860); Ordway: Am. J. Sci. (2) **23**, 220 (1857); cf., also, Rose: Pogg. Ann., **75**, 1 (1848); Wittstein: Jahresber., 321 (1850).

[31] Barfoed: J. prakt. Chem., **101**, 368 (1867).

[32] Kowalwsky: Inaugural Dissertation, Breslau (1902).

[33] "Die Absorption," 56, 393 (1910); Z. anorg. Chem., **23**, 111 (1900).

[34] Graham: Ann., **121**, 1 (1862).

we should expect the sol of α-oxide, formed by hydrolysis of a dilute solution of $SnCl_4$, gradually to assume the properties of the dilute hydrochloric acid solution of β-oxide, as observed by Fremy, Rose, Löwenthal,[35] and others.[36]

In the light of the experiments of van Bemmelen, it is unlikely that the amorphous masses obtained by Engel and others are definite chlorides. Further doubt is thrown on this by Biron,[37] who obtained products similar to Engel's meta and para chlorides, but found their composition to be indefinite.

Sulfuric and Nitric Acid. Sulfuric acid acts on both α- and β-oxide in much the same way as hydrochloric acid. Dilute nitric acid peptizes the freshly formed oxide quite readily, but the aged oxide is neither dissolved nor peptized by even the most concentrated acid. The aging of stannic oxide gel can be followed by observing the decrease in the peptizability of the oxide with time and with increasing temperature of precipitation.[38]

Phosphoric Acid. The adsorbing power of β-oxide for phosphoric acid deserves special mention, since a standard analytical procedure for separating this acid from mixtures consists in adding tin foil to the nitric acid solution, the resulting β-oxide carrying down the phosphoric acid.[39] For the complete precipitation of 1 mol of phosphoric acid, 6 to 7 atoms of tin must be present, according to Classen;[40] 7, according to Antony and Mondolfo;[41] and 13, according to Wölbling.[42] Mecklenburg[43] showed conclusively that the removal of phosphoric acid by precipitated stannic oxide was not due to the formation of a definite stannic pyrophosphate, but to adsorption, the amount of acid carried down depending not only on its concentration but also on the nature of the oxide. The adsorption isotherms of five oxides, prepared at different temperatures, showed a decreasing adsorption capacity with increasing temperature of formation. Krüger[44] claims

[35] J. prakt. Chem., **77**, 321 (1859).

[36] Barfoed: J. prakt. Chem., **101**, 368 (1867); Allen: J. Chem. Soc., **25**, 274 (1872); Lorenz: Z. anorg. Chem., **9**, 369 (1895).

[37] J. Russ. Phys.-Chem. Soc., **36**, 933 (1904).

[38] Weiser: J. Phys. Chem., **26**, 667 (1922).

[39] Reynoso: J. prakt. Chem., **54**, 261 (1851); Roscoe and Schorlemmer: "Treatise on Chemistry," **2**, 899 (1923); Reissig: Ann., **98**, 339 (1856); Girard: Compt. rend., **54**, 468 (1862).

[40] "Angew. Methoden anal. Chem.," **2**, 555 (1903).

[41] Gazz. chim. ital., **28**, 145 (1898).

[42] "Lehrbuch anal. Chem.," 405 (1911).

[43] Z. anorg. Chem., **74**, 215 (1912).

[44] Z. anal. Chem., **82**, 62 (1930).

to get a stannic-phosphoric acid, $SnO_2 \cdot P_2O_5 \cdot 8H_2O$, by the action of phosphoric acid on the freshly formed oxide, but he gives only the indefinite evidence of an analysis of a hydrous precipitate to support his claim.

Action of Alkalis

Dilute caustic alkalis carry both α- and β-oxide into solution. For a long time this solution was believed to take place by virtue of the formation of definite alkali stannates and metastannates, largely because evaporation of solutions of the freshly formed oxide in strong alkali yields definite crystals having the formula $M_2SnO_3 \cdot 3H_2O$[45] or $M_2Sn(OH)_6$.[46] However, if the solution of α-oxide in dilute alkali is not evaporated but treated with alcohol, a precipitate is formed, varying in composition from 5 to 17 mols of stannic oxide to 1 mol of potassium oxide, depending altogether on the relative amounts of the two substances in solution. In like manner, the precipitate obtained from a solution of β-oxide in alkali varies very widely, depending as it does on the conditions of formation.[47]

Many years ago, van Bemmelen[48] called attention to the colloidal nature of the solutions of both α- and β-oxides in alkalis. He agitated the same amounts of α-oxide with like volumes of cold dilute potassium hydroxide of various concentrations; when the concentration of alkali was less than $8.8K_2O$ to $100SnO_2$, the peptized oxide precipitated spontaneously, carrying down with it a greater part of the alkali. As is usual, the amount of potassium hydroxide adsorbed by a given amount of oxide varied with the temperature and concentration, and there was no indication of the formation of definite stannates. He thus accounted for the wide variation in the composition of the precipitate thrown out by alcohol from the colloidal solution of the α-oxide in alkali, as observed by Ordway and others.

Van Bemmelen obtained similar results with the more difficultly peptizable β-oxide. The first action of dilute sodium hydroxide was to produce an opalescent solution that, in itself, showed the oxide

[45] Ordway: Am. J. Sci. (2) **40**, 316 (1865); Marignac: Ann. mines (5) **15**, 277 (1859); Moberg: J. prakt. Chem., **28**, 230 (1843).

[46] Bellucci and Parravano: Z. anorg. Chem., **45**, 142 (1905); other hydrates are also known; Haeffely: Dinglers polytech. J., **144**, 66 (1857); Jonas: Chem. Zentr., 607 (1865).

[47] Fremy: Ann. chim. phys. (3) **12**, 460 (1844); **23**, 385 (1848); Rose: Pogg. Ann,, **75**, 1 (1848); **105**, 564 (1858); Weber: **122**, 358 (1864); Musculus: Compt. rend., **65**, 961 (1867); Moberg: Berzelius' Jahresber., **22**, 144 (1843).

[48] "Die Absorption," 57 (1910).

to be in the colloidal state. The relative amounts of oxide and alkali in the solution were varied widely; and, as with α-oxide, spontaneous precipitation took place the more rapidly, the greater the relative amount of stannic oxide. These colloids were coagulated by excess alkali, which was not the case with colloidal α-oxide. All the precipitated oxides contained adsorbed alkali in varying amounts, depending on the alkali concentration and the physical character of the precipitate.[49]

Some observations of Heinz[50] and of Franz[51] give some idea of the relative ease of peptization of different oxides by alkali. Heinz prepared a colloidal solution of an α-oxide in which the ratio $K_2O : SnO_2$ was 1 : 200; and Franz obtained colloidal β-oxides in which this ratio varied from 1 : 25 to 1 : 50. As is usual, the peptizing action of KOH is greater than that of NaOH, the precipitating power of K^+ ion being appreciably smaller than that of Na^+ ion.[52]

STANNIC OXIDE SOL

FORMATION

In the preceding paragraph we have seen that a freshly formed gel of stannic oxide is peptized by dilute alkali, giving a negative sol. Graham[53] first prepared a sol almost free from electrolytes by adding alkali to stannic chloride solution or hydrochloric acid to sodium stannate solution short of precipitation and dialyzing the resulting solutions. In both cases a gel was first formed on the dialyzer, but this went into colloidal solution again as the purification was continued. The sol was negatively charged, doubtless owing to the presence of a small amount of free alkali. Excess of the latter was removed by the addition of a few drops of tincture of iodine. As noted previously, Graham was able to boil the sol without precipitating it, thereby forming colloidal β-oxide. His preparations were fairly pure and so were readily coagulated by salts and acids.

Schneider[54] dialyzed the sol formed by adding ammonia to stannic chloride short of precipitation; and Zsigmondy[55] peptized with

[49] *Cf.* Wintgen: Z. physik. Chem., **103**, 238 (1923).

[50] Dissertation, Göttingen (1914).

[51] Dissertation, Göttingen (1913).

[52] Weiser: J. Phys. Chem., **26**, 424 (1922); *cf.* Collins and Wood: J. Chem. Soc., **121**, 2760 (1922).

[53] Phil. Trans., **151**, 213 (1861).

[54] Z. anorg. Chem., **5**, 82 (1894).

[55] Ann., **301**, 361 (1898).

ammonia the thoroughly washed oxide formed by hydrolysis of a dilute solution of stannic chloride. The amount of ammonia required was very small; in one experiment, a single drop containing approximately 0.03 g of ammonia sufficed for the peptization of 1.45 g of oxide. Any excess ammonia was removed by heating the colloid to boiling, thus doing away with the necessity for dialysis. Sols prepared in this way were negatively charged and were readily precipitated by electrolytes, particularly those having strongly adsorbed cations. The properties of the precipitated oxides lay between those of the typical α- and β-oxides, and Zsigmondy believed them to be mixtures of the two forms, the usual properties of each being modified by the presence of the other. This view is incorrect.

As previously noted, hydrous stannic oxide freshly prepared at room temperature, is readily peptized by dilute mineral acids; and the aged oxide is peptized by concentrated hydrochloric and sulfuric acids under suitable condition, but not by nitric acid. The sols are positively charged owing to preferential adsorption of hydrogen ion,[56] as evidenced by the low precipitation value of sulfate ion in the presence of considerable excess of hydrogen ion.[57] Biltz[58] obtained a fairly pure positive sol by dialysis of stannic nitrate prepared by metathesis of stannic chloride and lead nitrate. Dumanskii and Kniga[59] obtained negatively charged sols by peptization of stannic oxide gel with tartaric acid. Metallic tin melted in an electric arc furnace and blown with air gives very finely divided stannic oxide which can be peptized by 0.02 to 0.01 N HCl.[60]

CONSTITUTION

As we have seen, the ratio of stannic oxide to alkali in a stannic oxide sol may be 200 or more. The constitution of such a sol may be represented in the following way:

$$\left[\left(\boxed{x\mathrm{SnO_2}\cdot y\mathrm{H_2O}\cdot z\mathrm{NaOH}}\ \mathrm{OH}^-\right)_n\cdot n - q\mathrm{Na}^+\right] + q\mathrm{Na}.$$
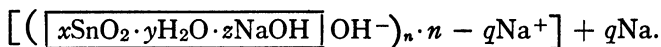
This indicates the varying composition of the colloidal particle and suggests that adsorbed hydroxyl ion constitutes the inner portion of

[56] *Cf.* Zocher: Z. anorg. Chem., 112, 46 (1920).

[57] Löwenthal: J. prakt. Chem., 56, 366 (1852); Mecklenburg: Z. anorg. Chem., 74, 207 (1912).

[58] Ber., 35, 4431 (1902).

[59] Kolloid-Z., 44, 273 (1928).

[60] Goldschmidt and Kohlschütter: British Pat. 189,706 (1922).

the double layer surrounding the particle and sodium ion the diffuse outer layer (*cf.* Vol. I, p. 86). Zsigmondy[61] and Wintgen[62] believe that the stabilizing electrolyte in such sols is sodium stannate instead of sodium hydroxide and represent the constitution

$$\boxed{x\text{SnO}_2 \cdot y\text{SnO}_3\text{HNa}} \quad z\text{SnO}_3\text{H}^- + z\text{Na}.$$
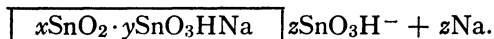
It is doubtful whether ammonium stannate is the stabilizing electrolyte when the sol is formed with ammonia, and there is no necessary reason for assuming the presence of sodium stannate in the sol peptized by alkali. For the sol prepared at 4° and analyzed by Wintgen's method (p. 57), Wintgen and Keilholz[63] found that particles 21 mμ in diameter contained 26,000 molecules of SnO_2, 1,300,000 molecules of H_2O, and 500 atoms of sodium on the inside; and 380 elementary charges compensated by 380 sodium atoms on the outside. A sol prepared at 80° contained 545,000 molecules of SnO_2 and 48,000,000 molecules of water and had 3150 elementary charges. Because of errors inherent in the experimental method of Wintgen, these values are probably much too high (p. 58).

In a sol peptized by tartaric acid and containing 7.4 g SnO_2 per l, the ratio of oxide to tartrate was found to be 243 after dialysis until neutral.[64]

PROPERTIES

Aging

The transformation of the freshly formed oxide peptized by hydrochloric acid into the so-called β-oxide has been followed in a number of ways, a few of which will be mentioned:

Löwenthal[35] found that potassium ferrocyanide could be removed from solution completely by the addition of a dilute solution of stannic chloride, but that the older the tin solution, the more was necessary to precipitate a definite amount of ferrocyanide and the greater was the relative amount of tin in the precipitate. This is shown in Table XIX. Löwenthal's observations were confirmed by Lorenz,[17] who assumed that the ferrocyanide was removed as SnFe(CN)_6, and that more old stannic chloride solution was necessary on account of the lower concentration of stannic ion resulting from slow hydrolysis. This explanation is unsatisfactory[65] for two reasons: first, because

[61] Z. anorg. Chem., **89**, 210 (1914).

[62] Kolloid-Z., **61**, 1 (1932); Z. physik. Chem., **103**, 238 (1922).

[63] Kolloid-Z., **55**, 323 (1931).

[64] Dumanskii and Kniga: J. Russ. Phys.-Chem. Soc., **60**, 229 (1928).

[65] Mecklenburg: Z. anorg. Chem., **64**, 372 (1909).

TABLE XIX

Age of SnCl$_4$ solution, days	Amount of SnCl$_4$ solution to precipitate 0.5 g K$_4$Fe(CN)$_6$, cubic centimeters	Composition of precipitate $\dfrac{\text{Mols of Sn(OH)}_4}{\text{Mols of K}_4\text{Fe(CN)}_6}$
0	6	1.5
7	10	2.3
14	14	3.3
89	27	6.5
126	32	7.5
162	36	8.5

the hydrolysis of inorganic salts takes place much more rapidly than Lorenz assumed; and, second, because the composition of the precipitate is not SnFe(CN)$_6$ but is variable, containing more and more tin the older the solution. The true explanation of Löwenthal's observations lies in the aging of the colloidal hydrous oxide. The addition of K$_4$Fe(CN)$_6$ causes coagulation of the sol. Since the particles of a newly formed sol are smaller and have a greater adsorption capacity than those of an older sol, less of the former is necessary to adsorb completely a given amount of ferrocyanide, and the ratio of tin to ferrocyanide in the precipitate is relatively low. As the sol ages, it becomes less stable, the adsorption capacity falls off so that more sol is necessary to adsorb a definite amount of ferrocyanide, and the ratio of tin to ferrocyanide becomes quite large.[66]

The age of stannic oxide sol may be determined roughly by treating with stannous chloride. The colloid prepared from newly formed stannic oxide is not precipitated by stannous chloride,[67] whereas the aged colloid is thrown down as a yellow precipitate by this reagent. The precipitate is variable in composition,[68] consisting of hydrous stannic oxide that has adsorbed varying amounts of stannous chloride under the different conditions of precipitation.[69] Collins and Wood observed a small increase in adsorption with increasing beta character of the hydrous oxide, indicating that some factor other than size of

[66] *Cf.* Barfoed: J. prakt. Chem., **101**, 368 (1867).

[67] Löwenthal: J. prakt. Chem., **77**, 321 (1859); Biron: J. Russ. Phys.-Chem. Soc., **36**, 933 (1904).

[68] Fremy: Ann. chim. phys. (3) **12**, 462 (1844); **23**, 393 (1848); Schiff: Ann., **120**, 47 (1861); Tschermak: J. prakt. Chem., **86**, 334 (1862).

[69] Weiser: J. Phys. Chem., **26**, 674 (1922); Collins and Wood: J. Chem. Soc., **123**, 452 (1923).

grain is involved.   As is usual, stannic oxide shows a stronger tendency to adsorb tin ions than chloride ions.   On account of the usual strong adsorption of hydrogen ion, the adsorption of stannous chloride is somewhat less in the presence of hydrochloric acid.[70]

It may be mentioned, in passing, that hydrogen sulfide precipitates stannous sulfide from a sol of the fresh oxide in dilute hydrochloric acid, whereas, from the aged sol, hydrogen sulfide precipitates hydrous stannic oxide that is converted only very slowly into stannous sulfide.[71] The explanation of this behavior is evident when we consider the difference in solubility of the new and old oxide.   In the new sol prepared by peptization with hydrochloric acid there is some stannic ion, the removal of which by precipitation as stannous sulfide results in further solution and subsequent precipitation until all is thrown down as sulfide, whereas the aged sol contains but a negligible amount of stannic ion and the precipitate with hydrogen sulfide is almost entirely the hydrous oxide.

It thus appears that we may have sols of any number of hydrous stannic oxides, each differing from the others in the size of the primary hydrous particles and, hence, in their reactivity, adsorbability, and stability under given conditions.   As a rule, the particles tend to agglomerate into denser and less reactive secondary aggregates on standing, but the reverse process goes on in the presence of fairly concentrated hydrochloric acid or alkali.   As with the precipitated oxide, there is no ground for assuming that the different sols are mixtures of colloidal α- and β-oxides in varying proportions.

Protective Action on Colloidal Metals

One of the most characteristic properties of colloidal stannic oxide is its protective action on colloidal metals.   It is well known that a gold solution treated with stannous chloride first gives a red coloration followed by the settling out of a purple or brown precipitate known as gold purple of Cassius, from its discoverer, Andreas Cassius, of Leyden (Vol. I, p. 47).   Because of its wide use as a pigment in the ceramic industry, a number of recipes have been given for its preparation.   The substance varies in color and composition with the method of formation.   Certain earlier investigators, as Richter and Gay-Lussac, believed purple of Cassius to be a mixture, but Berzelius

[70] Cf., however, Collins and Wood: J. Chem. Soc., 123, 452 (1923).
[71] Jörgensen: Z. anorg. Chem., 28, 140 (1901); Barfoed: J. prakt. Chem., 101, 368 (1867).

thought that it must be a definite compound. The latter view is supported by several facts: purple of Cassius is purple in color, whereas a mixture of gold and stannic oxide is brick red; gold is not separated from purple of Cassius with aqua regia, whereas it is from a mixture; mercury does not extract gold from the purple as it does from a mixture; and finally, the freshly prepared purple is dissolved by ammonia, forming a purple liquid. In spite of this evidence, we now know that Berzelius' view is incorrect. Debray[72] believed that gold forms a kind of color lake with stannic oxide, which is soluble in ammonia. Schneider[73] emphasized the colloidal character of the purple and concluded rightly that its ammoniacal solution is a mixture of colloidal gold with colloidal hydrous stannic oxide. Supporting Schneider's view, Zsigmondy[55] showed that a mere trace of ammonia will dissolve a large amount of freshly precipitated purple, and that this purple solution will not pass through parchment during electrolysis, as electrolytes do. He settled the question once for all by precipitating with nitric acid suitable mixtures of colloidal gold with colloidal stannic oxide, obtaining purples almost identical with those prepared in other ways. The gold does not combine chemically with stannic oxide, but the usual properties of the former are masked by the protective action of the latter.

Colloidal gold was found by Müller[74] to impart a red coloration to a number of substances,[75] and Moissan[76] obtained purples by distilling gold with tin, alumina, magnesia, zirconia, silica, and lime. Substances similar to gold purples have been prepared with other metals. Thus Wöhler[77] obtained silver purples similar to the gold pigment by mixing silver nitrate with stannous nitrate, and Lottermoser[78] prepared the former synthetically in the same manner as Zsigmondy prepared the latter. Wöhler[79] has also made an analogous platinum combination. All these so-called "purples" are colloidal in nature, the composition varying with the conditions of formation. Their colloid chemistry is chiefly that of the hydrous oxide. When freshly prepared, the purples are readily peptized by ammonia or dilute hydrochloric acid; but when dried, little or no pep-

[72] Compt. rend., **75**, 1025 (1872).

[73] Z. anorg. Chem., **5**, 80 (1894).

[74] J. prakt. Chem. (2) **30**, 252 (1884).

[75] Antony and Lucchesi: Gazz. chim. ital. (2) **26**, 195 (1896).

[76] Compt. rend., **141**, 977 (1905).

[77] Wöhler and Spengel: Kolloid-Z., **7**, 248 (1911).

[78] "Anorganische Kolloide," 53 (1901).

[79] Kolloid-Z., **2**, 2nd Supplement III (1907).

tizing action results even with concentrated ammonia or hydrochloric acid.

Coagulation

Coagulation by Electrolytes. Stannic oxide sol is much less hydrophilic than silica sol and is coagulated by low concentrations of electrolytes, especially if the cations are multivalent. ⌐ As already pointed out, Wintgen[80] believes that stannate ion is the stabilizing ion in the sol peptized by hydroxides. From coagulation experiments, he concludes that all electrolytes which form insoluble stannates will coagulate the sol in equivalent concentrations. It will be recalled that Duclaux reported equivalence in the precipitating power of several electrolytes for ferric oxide sol (p. 78). Actually the precipitating power of multivalent anions for ferric oxide sol is of a similar order of magnitude, but is not the same; and a careful determination of the precipitation values of electrolytes for stannic oxide sol would doubtless show that no two are exactly equivalent. Certainly the precipitating powers of barium and strontium chloride and hydrochloric acid are not equivalent, as Wintgen claims.[81]

During coagulation, the multivalent cation of the precipitating electrolyte undergoes exchange adsorption with the alkali or ammonia cation in the diffuse outer layer surrounding the particles. The mechanism of the exchange adsorption and its rôle in reducing the charge on the particles have been considered in detail in early chapters (pp. 76 and 112). Like Pauli, Wintgen formulates the process as a double decomposition reaction with the formation of an insoluble salt.

Mutual Action with Other Sols. Stannic oxide sol and positive sols undergo mutual coagulation in the usual way throughout a limited range.[82] On either side of the mutual coagulation zone, the sol in excess adsorbs the other and prevents it from coagulating. An interesting example of this behavior comes up in connection with the analytical determination of tin as stannic oxide in the presence of iron. Rose[83] observed that, when iron is present in small amounts, the stannic oxide precipitated from nitric acid solution is contaminated by it, but that when any considerable quantity of iron is present, both the iron and tin remain in solution. Lepéz and Storch[84] digested tin

[80] Kolloid-Z., **61**, 1 (1932).
[81] Weiser: J. Phys. Chem., **26**, 678 (1922).
[82] Weiser and Chapman: J. Phys. Chem., **35**, 543 (1931); **36**, 713 (1932).
[83] Pogg. Ann., **112**, 164 (1861).
[84] Monatsh., **10**, 283 (1889).

with nitric acid containing iron, and obtained solutions of variable stability depending on the relative amounts of the two metals present; solutions containing 2 atoms or less of tin to 1 of iron could be boiled and even evaporated to dryness in a vacuum. Concentrated nitric acid threw out of the solutions a yellowish precipitate that redissolved on dilution; sulfuric acid and sulfates caused a permanent precipitate; whereas acetic acid and alkali chlorides and nitrates caused no precipitation. By evaporating different solutions, Lepéz and Storch claimed to get compounds having such formulas as $1.8SnO_2 \cdot H_2O \cdot Fe_2O_3 \cdot 1.8N_2O_5$ and $4SnO_2 \cdot H_2O \cdot Fe_2O_3 \cdot 1.1N_2O_5$. When a mixture of hydrous ferric and stannic oxides was thrown down from the mixed nitrates by a slight excess of ammonia and the precipitate washed free from ammonium nitrate, this precipitate, still containing a trace of ammonia, dissolved in water to a clear solution. Removal of ammonia by dialysis resulted in precipitation; but the addition of a trace of ammonia again caused complete solution. Chromic nitrate behaved like ferric nitrate, but aluminum, uranium, cobalt, nickel, and copper nitrates did not cause solution of stannic oxide.

The phenomena described by Lepéz and Storch strongly suggest that their ferric-stannic mixtures were not salt solutions but were either colloidal solutions of hydrous ferric oxide peptized by hydrous stannic oxide or colloidal hydrous stannic oxide peptized by ferric and hydrogen ions. The real nature of the mixtures was shown by the following experiments:[81] Mixtures of freshly prepared oxides were treated with 100 cc. of 0.01 N NH$_4$OH as shown in Table XX. The results are quite conclusive. Hydrous stannic oxide is peptized by hydroxyl ion, whereas hydrous ferric oxide is not. However, the colloidal stannic oxide adsorbs ferric oxide and carries it into colloidal solution as long as tin is present in excess. At the same time, hydrous ferric oxide adsorbs stannic oxide and tends to take it out of colloidal solution so that no tin remains peptized when the former is present in large excess. This is quite analogous to the behavior of hydrous chromic oxide with the hydrous oxides of iron, manganese, cobalt, nickel, copper, and magnesium (p. 137).

It was shown further that ferric nitrate peptizes both newly formed and aged stannic oxide, whereas nitric acid does not peptize the aged oxide. Accordingly, if the freshly prepared oxide is peptized either (1) by ferric nitrate or (2) by a suitable mixture of the nitrate and nitric acid, coagulation will not take place on boiling on account of the stabilizing action of ferric oxide sol in (1) or of the adsorbed

cations in (2).   If in (2) the concentration of ferric ion in nitric acid solution is too low, partial coagulation takes place.

TABLE XX

PEPTIZATION OF MIXTURES OF HYDROUS STANNIC OXIDE AND
HYDROUS FERRIC OXIDE WITH 0.01 N NH$_4$OH

Mixed oxides prepared from N SnCl$_4$ + N FeCl$_3$, cubic centimeters		Observations
9.5	0.5	Clear colorless colloidal solution
9.0	1.0	Clear colloidal solution with yellow tinge
8.5	1.5	Clear yellow colloidal solution
8.0	2.0	Clear yellow colloidal solution
7.5	2.5	Clear reddish yellow colloidal solution
6.0	4.0	But little ferric oxide peptized; supernatant liquid cloudy
5.0	5.0	No ferric oxide peptized; supernatant liquid clear and colorless
2.0	8.0	No peptization of either hydrous oxide

STANNIC OXIDE JELLIES

The spontaneous evaporation of a stannic oxide sol gives a transparent jelly.   A jelly is also obtained by coagulation of a sufficiently concentrated sol with suitable amounts of electrolyte.   For example, the author[85] prepared firm transparent jellies by adding the precipitation concentration of barium chloride, strontium chloride, or hydrochloric acid to a sol containing 28 g SnO$_2$ per l.   If slightly higher electrolyte concentrations are used, a cloudy jelly or a gelatinous precipitate results.   If just the right amount of electrolyte is added, a thixotropic jelly is obtained which will be changed to a sol by shaking and will set to a jelly once more on standing (p. 23).

Stannic oxide precipitates directly in the form of a firm opaque jelly on mixing 20 cc of 1.4 M SnCl$_4$ with 3 cc of 3.5 N NaC$_2$H$_3$O$_2$, 1.7 cc of M (NH$_4$)$_2$SO$_4$, and 1.7 cc of 0.96 N NH$_4$OH.[86]

[85] Weiser: J. Phys. Chem., **26**, 681 (1922).
[86] Prakash and Dhar: J. Indian Chem. Soc., **6**, 391 (1929); **7**, 591 (1930).

HYDROUS STANNOUS OXIDE HEMIHYDRATE

The addition of alkali hydroxide or carbonate to a solution of stannous chloride precipitates a yellow gelatinous mass which proves to be hydrous stannous oxide hemihydrate.   Bury and Partington[87] prepared 5 different samples using ammonia, carbonate, and alkali as precipitants both in the air and in an atmosphere of carbon dioxide. With alkali and carbonate, the samples possessed a yellow tinge from the start, but with ammonia, they were white when first prepared, becoming yellow on drying.   After drying over phosphorus pentoxide the composition was said to correspond to $3SnO_2 \cdot 2H_2O$;[88] but the water content of the various samples varied from 7.11 to 8.82%, the
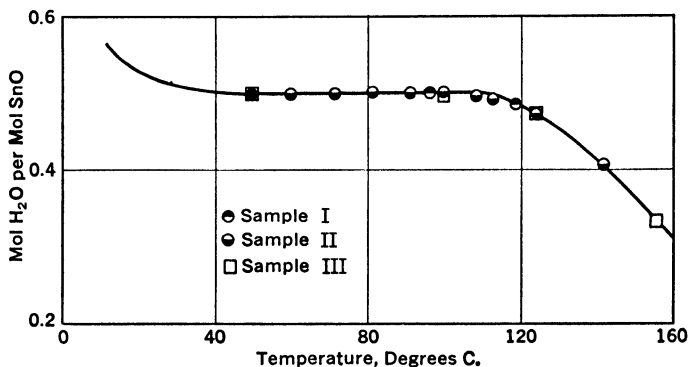
FIG. 42.—Dehydration isobar of $SnO \cdot 0.5H_2O$.

calculated value being 8.16%.   Since these data are insufficient to establish the identity of the alleged hydrate, Weiser and Milligan[89] ran the isobaric temperature-composition curve for three samples of the oxide precipitated from stannous chloride solution with ammonia and thoroughly washed.   The gelatinous precipitate is very difficult to wash free from the mother liquor, and if the washing is carried too far, peptization results.   Accordingly, the washing was carried out to incipient peptization using the ordinary centrifuge; and later the super-centrifuge was employed to obtain an almost chloride-free precipitate. This was air dried, and the isobar was run by heating the samples in a stream of nitrogen.   The curve, Fig. 42, shows that between 50 and 120° the composition is $SnO \cdot 0.5H_2O$.   Moreover, the compound gives

[87] J. Chem. Soc., **121**, 1998 (1922).

[88] *Cf.* Ditte: Ann. chim. phys. (5) **27**, 145 (1882); Straumanis and Strenk: Z. anorg. Chem., **213**, 301 (1933).

[89] J. Phys. Chem., **36**, 3039 (1932).

a definite x-ray diffraction pattern which is distinctly different from that of the black anhydrous α-stannous oxide or the grayish green anhydrous β-stannous oxide formed by heating α-stannous oxide to approximately 550°.[90] Dehydration of the hemihydrate at temperatures below 550° yields α-stannous oxide.

The white or pale yellow hemihydrate dried at room temperature, and the decidedly yellow preparation dried at 110°, give the same x-ray diffraction pattern; but the crystals of the deep yellow' product are the larger.

The hydrous hemihydrate loses water even in contact with water, going over to the black anhydrous state. This is accelerated by the presence of excess alkali and by the action of light, especially in the absence of free ammonia. Bury and Partington failed to observe dehydration with the accompanying color change in quartz, probably because they used an opaque vessel.[91] The color of the anhydrous oxide is blue-black in larger crystals and brownish green when powdered. Roth[92] and Fremy[93] claimed to get a cinnabar-red oxide, but this has not been confirmed.

The hydrous hemihydrate is dissolved by alkali forming $NaHSnO_2$ unless the alkali is quite concentrated when Na_2SnO_2 is obtained.[94] Schneider[54] reports the preparation of a sol of Sn_2O_3 by adding a very dilute solution of stannous chloride to a sol of hydrous stannic oxide and dialyzing in the absence of air. The sol is a yellow, clear, neutral liquid with strong reducing properties; thus, the addition of gold chloride gives gold purple. In all probability, the sol is not Sn_2O_3 but a mixture of hydrous stannic oxide and basic stannous chloride[95] stabilized by the hydrous oxide.

HYDROUS LEAD MONOXIDE

WHITE PRECIPITATED LEAD MONOXIDE

Formation

A hydrous precipitate of lead monoxide is formed by the addition of a base to a solution of lead salt. Ammonium hydroxide is better than alkalis and lead acetate better than lead nitrate since alkali

[90] Weiser and Milligan: J. Phys. Chem., **36**, 3039 (1932); Keysselitz and Kohlmeyer: Metall u. Erz, **30**, 185 (1933).

[91] *Cf.* Weiser and Milligan: J. Phys. Chem., **36**, 3039 (1932).

[92] Ann., **60**, 214 (1846).

[93] Ann. chim. phys. (3) **12**, 460 (1844); **23**, 385 (1848).

[94] Hantzsch: Z. anorg. Chem., **30**, 289 (1902); Goldschmidt and Eckardt: Z. physik. Chem., **56**, 385 (1906); Koelichen: **33**, 129 (1900).

[95] Carson: J. Am. Chem. Soc., **41**, 1969 (1919).

cations and nitrate anions are adsorbed so strongly that they cannot be removed even by prolonged washing. Kohlschütter[96] prepared a product free from adsorbed electrolytes by the addition at $0°$ of lead acetate (185 g in 1 l of CO_2-free water) in a jet to 1 l of 14 N NH_4OH, followed by washing the white crystalline precipitate a number of times by decantation with CO_2-free water. Pleissner[97] obtained an equally pure product by the interaction of lead acetate and barium hydroxide.

The oxide is obtained in the sol state by dialysis of a solution of lead tartrate.[98]

Composition

The white precipitate is a hydrous hydrate, the formula of which is given as $2PbO \cdot H_2O$, $2.5PbO \cdot H_2O$, and $3PbO \cdot H_2O$ by different investigators. Since the theoretical percentage of lead is 89.22, 89.93, and 90.39, respectively, it is rather difficult to say who is right. A sample prepared by Hüttig and Steiner,[99] using Kohlschütter's method and drying in a vacuum desiccator containing 30% KOH for 1 day, analyzed for $PbO \cdot 0.504H_2O$. This preparation was sealed up for a month, and the composition did not change. The dehydration isobar for a hydrous preparation of the composition $PbO \cdot 1.218H_2O$ showed a "flat" corresponding to $2PbO \cdot H_2O$.[100] On the other hand, Randall and Spencer[101] dried to constant weight in a vacuum desiccator over sulfuric acid, a precipitate formed by Pleissner's method, and the analysis showed it to be almost exactly $2.5PbO \cdot H_2O$, in accord with the observations of Glasstone[102] and of Töpelmann;[103] but Randall and Spencer stick to Pleissner's formula $3PbO \cdot H_2O$.[104] Until there is some conclusive evidence to the contrary, the author prefers to think of the compound as a hemihydrate like the corresponding tin compound. Be that as it may, the important thing is that the white precipitate is a hydrous hydrate which gives a distinctive

[96] Kohlschütter and Roesti: Ber., **56B**, 275 (1923).

[97] Arb. kais. Gesundh., **26**, 384 (1907).

[98] Dumanskii and Buntin: J. Russ. Phys.-Chem. Soc., **60**, 933 (1928).

[99] Z. anorg. Chem., **197**, 257 (1931).

[100] *Cf.* Schaffner: Ann., **51**, 175 (1844); Ogata and Kaiun: J. Pharm. Soc. (Japan) **492**, 75 (1923).

[101] J. Am. Chem. Soc., **50**, 1572 (1928); Spencer and Mote: **54**, 4618 (1932).

[102] J. Chem. Soc., **119**, 1914 (1921).

[103] J. prakt. Chem. (2) **121**, 320 (1929).

[104] *Cf.* Payen: Ann. chim. phys. (4) **8**, 302 (1866); Lorenz: Z. anorg. Chem., **12**, 436 (1897); Böttger: Z. physik. Chem., **46**, 585 (1903).

x-radiogram entirely different from the patterns obtained with the yellow or red anhydrous oxides.

As long as the precipitated oxide contains more water than corresponds to the hemihydrate, it is white in color, but as soon as the water content falls below this point, it become slightly colored and the x-ray pattern shows some of the lines of the yellow oxide.[99]

Chemical Properties

Lead oxide dissolves slightly in dilute alkali but appreciably in concentrated alkali,[105] forming plumbite.[106]   The alkali plumbites are
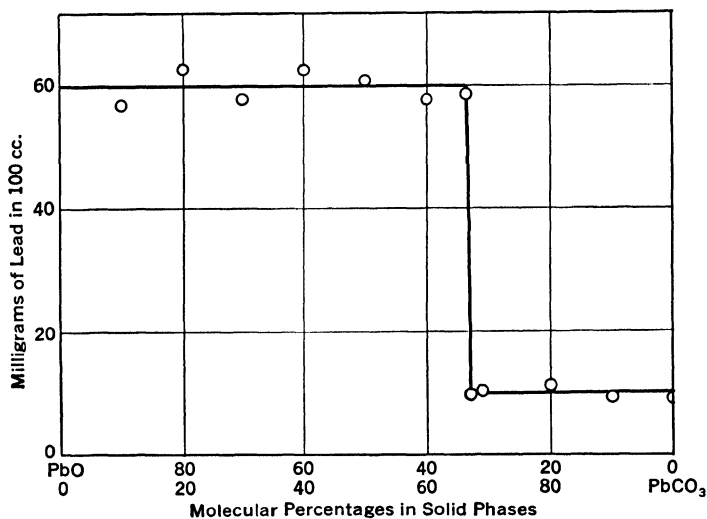
FIG. 43.—Composition of white lead.

strongly adsorbed by cotton.   By washing the fiber thoroughly, the salts are hydrolyzed, giving alkali that dissolves out and lead oxide that is retained by the fiber and acts as a mordant.[107]

Although the compound $Pb(OH)_2$ is not known, it is an interesting fact that boiling lead sulfate or chloride with aqueous sodium carbonate gives $Pb(OH)_2 \cdot 2PbCO_3$, basic lead carbonate or white lead.[108] The same compound is formed by bringing anhydrous lead oxide and lead carbonate together in a sodium acetate solution.   In Fig. 43

[105] Berl and Austerweil: Z. Elektrochem., **13**, 165 (1907).
[106] Hantzsch: Z. anorg. Chem., **30**, 305; Herz and Fischer: **31**, 454 (1902).
[107] Bonnet: Compt. rend., **117**, 518 (1893).
[108] Salvadori: Gazz. chim. ital., **34** I, 87 (1904).

are given the results of allowing various mixtures of lead oxide and lead carbonate to stand in contact with 20% $NaC_2H_3O_2$ solution at 75° for 12 hours and subsequently analyzing both solutions and precipitates.[109]   The diagram shows that the lead oxide and lead carbonate do not form solid solutions but a compound containing 1 mol of the former to 2 of the latter.   Water determinations show the formula to be $Pb(OH)_2 \cdot 2PbCO_3$.[110]

RED AND YELLOW LEAD MONOXIDES

Lead monoxide occurs in nature in two crystalline forms: litharge and massicot, which are yellow and red, respectively.   The white precipitated oxide is converted into the yellow oxide by boiling with 5 M alkali, and this in turn is converted into the stable·red form by boiling with 12 M alkali.[111]   The transformation to red is more rapid and requires a lower concentration of alkali if the lead acetate solution is precipitated directly with hot alkali.   During isobaric dehydration, the white hemihydrate passes through brown to red as the temperature is raised, the cinnabar-red color appearing at temperatures around 120° and above.

The difference between the yellow and red oxides, prepared as described above, is due to difference in crystal structure.   Glasstone[112] attempted to show that the relationship between the two is closer than that of allotropy.   He calls attention to the transformation of all red forms to brownish yellow on grinding, and all yellow forms to red on heating with concentrated alkali.   The observations indicate a close connection between color and size of particles, the large particles appearing red and the small ones yellow.   In further support of this view, Glasstone[112] made solubility determinations, both gravimetric and electrometric, on eight different preparations varying in color from lemon yellow through reddish brown to red, and found approximately the same value, irrespective of the color.   Microscopic examinations likewise indicate that the red forms are made up of larger particles, the yellow samples being agglomerates of small particles which are almost identical with the finely divided red forms. These data are misleading, however, as Applebey and Reid[113] suc-

[109] Hawley: J. Phys. Chem., 10, 654 (1906).

[110] *Cf.* Pleissner: Arb. kais. Gesundh., 26, 384 (1907).

[111] Geuther: Ann., 219, 56 (1883); Ruer: Z. anorg. Chem., 50, 265 (1906); Applebey and Reid: J. Chem. Soc., 121, 2129 (1922).

[112] J. Chem. Soc., 119, 1689, 1914 (1921).

[113] J. Chem. Soc., 121, 2129 (1922).

ceeded in making well-defined crystals of the two forms which differ not only in crystal structure but also in solubility, the yellow being 1.8 times as soluble as the red.[114]   Glasstone's products were mixtures, and the constant solubility he observed was the value for the more soluble yellow form.   Applebey and Reid's conclusions were confirmed by Kohlschütter and Scherrer,[115] Hüttig and Steiner,[99] and Darbyshire,[116] who examined the two forms with x-rays and found them structurally different, the yellow being orthorhombic[117] and the red hexagonal.[118]   Darbyshire showed that the color variation in commercial lead monoxides is due in part to variations in particle size, as Glasstone suggested, and in part to the fact that they are usually mixtures of the two crystalline forms.   Commercial red lead is usually contaminated with the yellow but seldom with the red oxide.   The black color of certain specimens of lead monoxide is due to the presence of metallic lead in the preparation,[119] the action of heat and light causing blackening of either the yellow or red oxide in the presence of alkali.

HYDROUS LEAD PEROXIDE

Electrolysis of a weak alkaline solution of lead sodium tartrate gives a black lustrous deposit which Wernicke[120] believed to be $PbO_2 \cdot H_2O$ or H_2PbO_3, metaplumbic acid.   The alleged hydrate is said to form also during the electrolysis of sodium chloride solution in which litharge is suspended; but Wernicke reports the formation of lead peroxide with variable quantities of water by electrolyzing dilute solutions of lead nitrate for varying lengths of time.

Well-defined metaplumbates and orthoplumbates, corresponding to the hypothetical acid H_4PbO_4 or $PbO_2 \cdot 2H_2O$, are well known. According to Bellucci and Parravano,[121] the metaplumbates such as $K_2PbO_3 \cdot 3H_2O$ should be regarded as salts of an acid $H_2Pb(OH)_6$, both because of isomerism with the corresponding stannate and platinate and because they cannot be dehydrated without decomposition.   The salts hydrolyze slowly in water and more rapidly in acid

[114] Cf. Randall and Spencer: J. Am. Chem. Soc., **50**, 1572 (1928).

[115] Helv. Chim. Acta, **7**, 337 (1924).

[116] J. Chem. Soc., 211 (1932).

[117] Halla and Pawlek: Z. physik. Chem., **128**, 49 (1927).

[118] Dickinson and Friauf: J. Am. Chem. Soc., **46**, 2457 (1924); van Arkel: Rec. trav. chim., **44**, 652 (1925).

[119] Applebey and Powell: J. Chem. Soc., 2821 (1931).

[120] Pogg. Ann., **141**, 109 (1870).

[121] Z. anorg. Chem., **50**, 107 (1906); Atti accad. Lincei, **14** I, 378, 457 (1905).

to give hydrous lead peroxide. Simon[122] ran the dehydration isobar for samples of the peroxide formed (1) by Wernicke's method and (2) by decomposition of sodium metaplumbate by hydrocyanic acid. From the curves which are reproduced in Fig. 44, it is apparent that the water carried down by the oxide is adsorbed and no hydrates are formed.
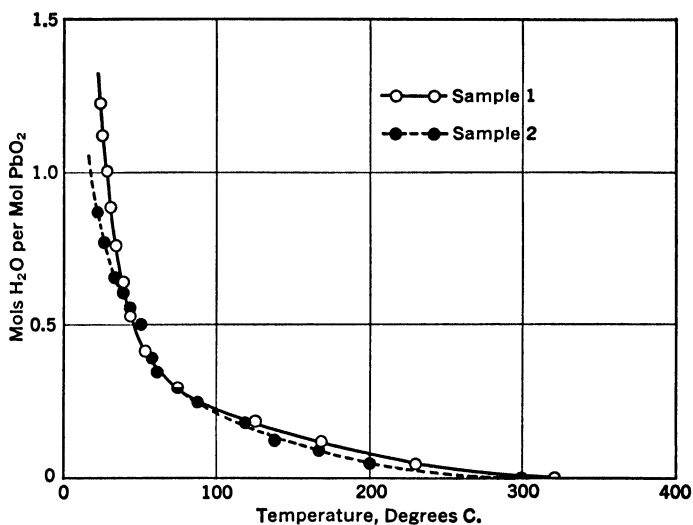
FIG. 44.—Dehydration isobars of hydrous PbO$_2$.

LEAD PEROXIDE SOL

The alkali formed by the slow hydrolysis of a solution of sodium metaplumbate may be removed by dialysis, leaving a sol of lead peroxide which is fairly stable if the dialysis is not carried too far. Bellucci and Parravano[123] observed that a sol containing 0.32 g PbO$_2$ and 0.008 g K$_2$O, that is, 175 mols of peroxide to 1 of alkali, is neutral in reaction and gives no depression of the freezing point of water. It possesses a chestnut-brown color, and is perfectly clear in transmitted light but cloudy by reflected light; it can be diluted, heated to boiling, frozen, and evaporated on the water bath without coagulation. By evaporating the excess water, a jelly is formed which can be repeptized by water; drying the jelly renders it non-peptizable. The sol is negatively charged and is quite sensitive to the action of

[122] Z. anorg. Chem., **185**, 280 (1930).
[123] Atti accad. Lincei, **15** II, 542, 631 (1906).

certain electrolytes, particularly those having multivalent cations. The order of precipitating power of chlorides is: $Fe > Al > Ca > Sr > Ba > Mg > Cd > Hg > Mn > Ni > Co > Cu > NH_4 > Cs > Li > K > Rb > Na$. The effect of stabilizing ions having the same charge as the sol is quite marked. Thus the potassium salts of AsO_4, CO_3, C_2O_4, and IO_4 do not coagulate the sol; $Fe(CN)_6^{III}$, ClO_4, ClO_3, MnO_4, Cr_2O_7, Br, Cl, CNS, SO_4, NO_3, IO_3, and $C_2H_3O_2$ precipitate it partially; and F, $C_4H_4O_6$, $Fe(CN)_6^{IV}$, and I precipitate it completely. The cause of the relatively slight stabilizing action of ferrocyanide and tartrate ions should be investigated.

HYDROUS LEAD SESQUIOXIDE

The addition of sodium hypochlorite to a solution of lead monoxide in alkali is said to yield a compound having the formula $Pb_2O_3 \cdot 3H_2O$,[124] but Glasstone claims that it is a mixture of the above compound with $2PbO \cdot H_2O$. The orange-yellow precipitate formed by mixing solutions of alkali plumbate and plumbite (PbO in alkali) is also said to yield $Pb_2O_3 \cdot 3H_2O$[125] when dried over sulfuric acid and $Pb_2O_3 \cdot 2H_2O$ when dried between 170–190°. Glasstone claims to get a purer product by precipitating the alkali plumbate-plumbite mixture with acetic acid, followed by redissolving the precipitate in alkali and reprecipitating until the ratio of PbO_2 to PbO in the compound is unity. Darbyshire[116] examined preparations obtained by both of the above methods with the x-rays, but neither gave any indication of a diffraction pattern. On heating to 400°, they gave yellow lead monoxide.

No hydrate or hydrous form of Pb_3O_4 is reported.

[124] Winkelblech: Ann., **21**, 21 (1837).
[125] Seidel: J. prakt. Chem. (2) **20**, 200 (1879); *cf.* Bellucci and Parravano: Z. anorg. Chem., **50**, 107 (1906).

CHAPTER IX

THE HYDROUS OXIDES OF TITANIUM, ZIRCONIUM, AND THORIUM

The hydrous oxides of titanium, zirconium, and thorium are always described as existing in both an alpha or ortho and a beta or meta modification. In every case the relationship between these two forms is the same as between the so-called α- and β-stannic oxides whose colloid chemistry has been considered in detail in the preceding chapter. Accordingly, in this chapter will be given but a brief survey of this phase of the chemistry of the hydrous oxides under consideration.

HYDROUS TITANIUM DIOXIDE

PRECIPITATED TITANIA

Formation

The product commonly called orthotitanic acid or α-titanic acid is a white gelatinous precipitate formed by the addition of ammonia or alkali hydroxide to a solution of a tetravalent titanium salt. The highly hydrous gel is readily soluble in dilute acids and is easily peptized by dilute alkalis and suitable salts to give stable sols. If heated rapidly the oxide exhibits the glow phenomenon; but as usual, if the heating is slow or the temperature is held for some time below the glow temperature, a gradual sintering and loss of surface energy takes place without incandescence.

The product referred to as metatitanic acid, or β-titanic acid, is a granular, difficultly soluble, and but slightly peptizable substance which does not exhibit the glow phenomenon under any circumstances. It is obtained (*a*) by the interaction of nitric acid and titanium, (*b*) by aging under water of the so-called α-titanic acid slowly in the cold and more rapidly in the hot, (*c*) by precipitation in the hot, and (*d*) by hydrolysis of boiling solutions of tetravalent titanium salts. The oxide formed by hydrolyzing the chloride cannot be washed without undergoing peptization as a positive sol, but the oxide from sulfate is not peptized by washing on account of the precipitating power of sulfate ion.

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Composition

The composition of the preparation referred to above varies with the procedure employed. The thermal dehydration isobars of both the fresh and the aged oxides are smooth curves indicating that the formulas corresponding to the acids assumed by earlier investigators[1] were obtained by drying under arbitrary conditions.[2] This was confirmed by Weiser and Milligan[3] from x-ray analysis of precipitates

1	PRECIPITATED AT ROOM TEMPERATURE
2	Ti_2O_3 x H_2O OXIDIZED IN THE AIR
3	NO. 1 AGED 30 WEEKS AT ROOM TEMP.
4	NO. 1 HEATED TO 184°
5	NO. 1 AGED 6 HOURS AT 100°
6	PRECIPITATED AT 100°
7	HYDROLYSIS OF $Ti(SO_4)_2$
8	MINERAL ANATASE, TiO_2
9	HYDROLYSIS OF $TiCl_4$ OR $Ti(NO_3)_4$
10	MINERAL RUTILE, TiO_2
11	NO. 1 HEATED TO 1000°
12	NO. 2 HEATED TO 1000°
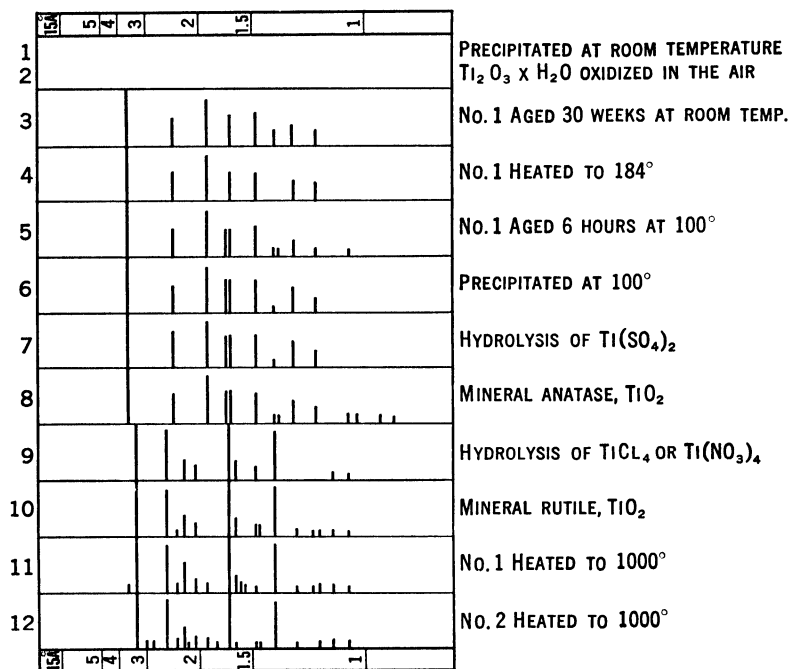
FIG. 45.—Diagrams of the x-ray diffraction patterns of titanium oxides.

prepared and aged to give the so-called α- and β-acids. The data are summarized in chart form in Fig. 45. From these results it is apparent that both "acids" really consist of anhydrous TiO_2 and adsorbed water. The oxide freshly formed in the cold gives no x-ray

[1] Gutbier, Ottenstein, Leutheusser, Lossen, and Allam: Z. anorg. Chem., **162**, 87 (1927).

[2] Rose: Ann., **53**, 267 (1845); Tüttschew, **141**, 111 (1867); Demoly: **72**, 259 (1849); Merz: J. prakt. Chem., **99**, 157 (1866); Weber: Pogg. Ann., **120**, 287 (1863); Wagner: Ber., **21**, 960 (1888).

[3] J. Phys. Chem., **38**, 513 (1934).

diffraction pattern. On standing in the cold for several weeks, it retains the properties of the α-oxide but gives the x-ray pattern corresponding to the mineral anatase. The same pattern is obtained with the so-called β-oxide formed by precipitating or aging of the α-preparation at 100° and by hydrolysis of $Ti(SO_4)_2$ at 100°. Curiously enough, the oxides formed by hydrolysis of $TiCl_4$ and $Ti(NO_3)_4$ give patterns corresponding to the mineral rutile, which is the stable modification of titania since heating the anatase form above 1000° gives the rutile modification.

The aging of the freshly formed oxide is a continuous process which can be followed by observing the decrease in the adsorption capacity for dyes and the falling off in the solubility and peptizability in hydrochloric acid.[4] There seems no experimental justification for assuming, as Morley and Wood do, that the change in physical character of the gelatinous oxide on aging is due to the formation of complex salt-like condensation products by the molecules of the hydrous oxide functioning both as acid and base.

Applications

Hydrous titanium dioxide probably finds its most important use as a mordant. If leather or textile goods are immersed in a solution of titanium salt and then steamed, the hydrous dioxide is precipitated. This adsorbs certain dyes, forming permanent, brilliantly colored lakes. As a mordant for alizarin orange, coerulein, and alizarin blue, titania is superior to chrome.[5] For delicate fabrics, titanium salts of organic acids are employed in order to avoid the injurious action of mineral acids. Both trivalent and tetravalent salts are used for this purpose.

If anhydrous titanium tetrachloride is sprayed into air, it takes up moisture, giving a dense smoke composed of fine particles of the solid hydrate, $TiCl_4 \cdot 5H_2O$. The chloride was used successfully during the world war for producing smoke screens. If the air is too moist, hydrolysis takes place, giving hydrochloric acid and hydrous titanium dioxide, which forms a smoke, but with less obscuring power than the chloride hydrate. The cloud may be increased in moist air by the presence of ammonia, which forms ammonium chloride. If the air is not very moist, however, ammonia must be avoided; otherwise the chloride forms an ammonate, $TiCl_4 \cdot 6NH_3$, which has little obscuring

[4] Morley and Wood: J. Soc. Dyers Colourists, **39**, 100 (1923); J. Chem. Soc., **125**, 1626 (1924).

[5] Barnes: J. Soc. Chem. Ind., **15**, 420 (1896); J. Soc. Dyers Colourists, **35**, 59 (1919); Hummel: **20**, 65 (1904).

power. On this account it is usually planned to disperse the tetrachloride and ammonia separately.

Anhydrous titania for use as a pigment is prepared by igniting the oxide formed by hydrolysis of titanic sulfate. Hixson and Plechner,[6] who have made a study of the hydrolysis reaction, find that a sulfate solution containing 6–10% TiO_2 is more than 95% precipitated by boiling 8 hours when the ratio of excess sulfuric acid to titanium oxide is one or less than one.

TITANIA JELLY

Titania like silica is easily obtained in the jelly state. More than a century ago, Rose[7] reported the formation of a soft titania jelly. He treated a fusion of titania and sodium carbonate with hydrochloric acid, filtered the solution, and allowed it to stand, whereupon the hydrous oxide aged and precipitated out a jelly. Later, Knop[8] obtained a jelly in an interesting way: A strong hydrochloric acid solution of magnetic oxide of iron was treated with tartaric acid and then neutralized with ammonia. The iron remained in solution, and the titania came down as a white precipitate. On filtering and attempting to wash the oxide, it swelled up in much the same manner as gelatin, forming a colorless transparent jelly which was transformed into a gelatinous precipitate by heating. Klosky and Marzano[9] prepared firm transparent jellies by neutralizing slowly an acid solution of titanium dioxide with the carbonate of sodium, potassium, or ammonium. Jellies also result by dialysis of an acid solution of titanium tetrachloride[10] and by hydrolysis of titanium tetraethyl.[11] The water in an aged jelly can be replaced by alcohol, ether, benzene, glycerol, or concentrated sulfuric acid in the same way as in the corresponding silica jelly.

TITANIA GEL

Titania forms an adsorbent gel similar to silica gel when the jelly prepared by the method of Klosky and Marzano is washed, dried, and activated at temperatures around 300–330°.[12] Although the Silica

[6] Ind. Eng. Chem., **25**, 262 (1933).

[7] Gilbert's Ann., **73**, 76 (1823); cf. Pfordten: Ann., **237**, 213 (1887).

[8] Ann., **123**, 351 (1862).

[9] J. Phys. Chem., **29**, 1125 (1925).

[10] Graham: Phil. Trans., **151**, 213 (1861); Bhatia and Ghosh: J. Indian Chem. Soc., **7**, 687 (1930).

[11] H. and W. Brintzinger: Z. anorg. Chem., **196**, 44 (1931).

[12] Cf. Klosky and Woo: J. Phys. Chem., **32**, 1387 (1928).

Gel Corporation have patented processes for making a good titania adsorbent, it is not likely to displace silica gel, which is, in general, easier to prepare, has a higher adsorption capacity, and is a better catalyst supporter than titania gel.[13] From observation on the adsorption of sulfur dioxide at −25, 0, 25, and 50°, Klosky and Burggraff[14] concluded that the phenomena over the entire pressure range could be interpreted best as a polymolecular layer adsorption;[15] the capillary theory is applicable only at lower pressures. It will be recalled that Urry found the capillary theory applicable to the adsorption of a number of gases by silica gel only at low relative pressures (p. 209). The adsorption of mixtures of sulfur dioxide and methyl chloride and of sulfur dioxide and butane[16] can be indicated quite accurately by the simple expression: $\dfrac{N_0 - N}{N_0} \div \dfrac{N_1' - N'}{N_0'} = \dfrac{M_2 \eta_2}{M_1 \eta_1}$, in which N and N' represent respectively the number of mols of the first and second components of the gas mixture adsorbed per gram of gel, and N_0 and N_0' the corresponding amounts adsorbed from the gas-air mixtures; M_1 and η_1 and M_2 and η_2 are the molecular weights and viscosities, respectively, of the two components.

Titania adsorbs the phosphate radical so strongly from alkali phosphates that it is no longer available to plants.[17] This may be of considerable economic importance because of the general distribution of titania in soils.

TITANIA SOL

Graham prepared a hydrous titania sol by dialysis of a 1% solution of the oxide in dilute hydrochloric acid.

Bhatia and Ghosh[18] prepared a sol containing 15 g TiO_2 per l by dropping titanium tetrachloride slowly into water at 18° followed by dialysis. Gutbier obtained it by hydrolysis of titanium trichloride solutions and oxidizing in a current of air. A better method consists in the peptization of the hydrous oxide with tartaric acid followed by dialysis. In this way a relatively pure sol was obtained in which the ratio, mols of titanium dioxide : mols tartrate, was 105.

[13] Klosky: J. Phys. Chem., **34**, 2621 (1930); cf. Nikitin and Jurjev: Z. anorg. Chem., **171**, 281 (1928).

[14] J. Am. Chem. Soc., **50**, 1045 (1928).

[15] Polanyi: Ber. deut. physik. Ges., **18**, 55 (1916); Berényi: Z. physik. Chem., **94**, 628 (1920).

[16] Klosky and Woo: J. Phys. Chem., **32**, 1387 (1928).

[17] Ungerer: Z. Pflanzenernähr. Düngung Bodenk., **21A**, 129 (1931).

[18] J. Indian Chem. Soc., **7**, 687 (1930).

Probably the most satisfactory method of preparing the sol consists in hydrolysis of titanic sulfate, washing the hydrous oxide free from sulfate with ammonia, and finally peptizing with as small an amount of hydrochloric acid as possible. In this way Freundlich and Kross[19] prepared sols containing 440 to 640 g per 1 of titanium dioxide, anatase modification. If the sols are sufficiently pure they remain in the sol state indefinitely, but if they contain too much electrolyte they are thixotropic, setting to jellies which are again converted into sols by shaking. The non-thixotropic sols can be made thixotropic by adding a small amount of electrolyte. The surface tension of even the most concentrated sol is the same as for pure water.

In sols formed by peptization with hydrochloric acid both H^+ and Ti^{++++} are the stabilizing ions. The sols are therefore positively charged and behave toward electrolytes like typical hydrophobic sols,[20] the precipitating power of the anions being in the order: $Fe(CN)_6^{IV} > Fe(CN)_6^{III} > OH > SO_4 > Cr_2O_7 > CrO_4 > IO_3 > S_2O_3 > NO_3 > Cl > Br$. Sodium hydroxide coagulates in low concentrations, but with somewhat higher concentrations the charge on the particles is reversed and a stable negative sol is obtained.

HYDROUS TITANIUM SESQUIOXIDE

The hydrous oxide of divalent titanium is thrown down as a black precipitate by adding hydroxyl ion to a solution of titanous salt. It is very unstable in the air, oxidizing first to blue hydrous titanium sesquioxide and finally to the white dioxide.

The hydrous oxide of trivalent titanium has been variously described as black, dark blue, cherry red, and brown-red, depending upon the exact conditions of formation. It is prepared by digesting a solution of dioxide in hydrochloric acid with metallic copper at 20 to 40° until the solution attains a violet-blue color, followed by the addition of ammonia. It is also thrown down directly from titanium trichloride solution with ammonia. If the hydrous oxide is shaken with milk of lime in the presence of oxygen, it is oxidized to the dioxide and, at the same time, an equivalent amount of hydrogen peroxide is formed. In the same way, when the sesquioxide is oxidized by a solution of chromic acid in the presence of potassium iodide, or

[19] Kolloid-Z., **52**, 37; Freundlich and Tamchyna: **53**, 288 (1930); Blumenfeld: U. S. Pat. 1,851,487 (1928).

[20] Freundlich and Kross: Kolloid-Z., **52**, 37; Freundlich and Tamchyna: **53**, 288 (1930); Bhatia and Ghosh: J. Indian Chem. Soc., **7**, 687 (1930); *cf.* Majumdar: **6**, 357 (1929).

by potassium permanganate in the presence of tartaric acid, hydrous titanium dioxide is formed, and simultaneously, oxidation of the potassium iodide or tartaric acid is brought about.[21] These are typical cases of auto-oxidation.[22]

HYDROUS TITANIUM PEROXIDE

The addition of hydrogen peroxide to a neutral or acid titanium solution produces an intense yellow coloration, owing to the formation of a hexavalent titanium compound. Since the color is quite distinct, even in the presence of less than 0.01% of titanium, the reaction affords a delicate test both for titanium and hydrogen peroxide.[23] If gelatinous titanium is treated with an excess of hydrogen peroxide, it is converted into yellow titanium peroxide. The latter compound is best obtained by dropping titanium tetrachloride slowly into dilute alcohol, adding a large excess of hydrogen peroxide, and finally, treating with ammonia, ammonium carbonate, or alkali.[24] The yellow hydrous oxide adsorbs salts so strongly that it is difficult to obtain pure.[25] When freshly formed, the composition can be represented by the formula $TiO_3 \cdot xH_2O$, but on drying over phosphorus pentoxide, it becomes a horny mass containing less oxygen than corresponds to a trioxide. Schwarz and Sexauer[26] believe the compound to be $TiO_2 \cdot O \cdot 2H_2O$. Since they used the Willstätter method to estimate the "hydrate" water, this part of the formula cannot be correct. The freshly precipitated hydrous peroxide appears to be considerably more soluble in alkali than the dioxide. This may be due in part to peptization since the alkali peroxide solutions are instable, depositing an aged granular oxide in the course of a few days. It is usually assumed, however, that the alkali solutions contain alkali pertitanate.[27]

[21] Manchot and Richter: Ber., **39**, 320, 488 (1906); Manchot and Wilhelms: Ann., **325**, 105 (1902); Haber: Z. Elektrochem., **7**, 441 (1900).

[22] Schönbein: J. prakt. Chem., **93**, 24 (1864); Traube: Ber., **26**, 1471 (1893); van't Hoff: Z. physik. Chem., **16**, 411 (1895); Engler and Wild: Ber., **30**, 1669 (1897).

[23] Richarz and Lonnes: Z. physik. Chem., **20**, 145 (1896); Haber and Grinberg: Z. anorg. Chem., **18**, 37 (1898).

[24] Levy: Compt. rend., **110**, 1368 (1890); Ann. chim. phys. (6) **25**, 433 (1892).

[25] Classen: Ber., **21**, 370 (1888); cf. Weller: **15**, 2592 (1882).

[26] Ber., **60B**, 500 (1927).

[27] Melikov and Pissarjewski: Ber., **31**, 678, 953 (1898); Z. anorg. Chem., **18**, 59 (1898); cf. Billy: Compt. rend., **172**, 1411 (1921).

HYDROUS ZIRCONIUM DIOXIDE
PRECIPITATED ZIRCONIA

Formation and Composition

The most gelatinous form of hydrous zirconia is obtained by precipitating a solution of a zirconium salt with ammonia or alkali.   The latter is adsorbed so strongly that the former must be used if a pure gel is desired.   When formed in the cold the precipitate is more gelatinous and more reactive than when formed in the hot.   Either preparation heated to approximately 300° glows brightly provided the water content is not reduced below 1.9%.[28]   If the hydrous mass is heated rapidly above 300°, the glowing is accompanied by small explosions, caused, in all probability, by expulsion of some of the adsorbed water.   It is an interesting fact that the oxide contains considerable water even after the glowing.   Ruer looks upon the glow phenomenon as a manifestation of the transformation of ordinary zirconia into isomeric metazirconia, but as we have seen, Wöhler[29] showed it to result from a sudden diminution in surface energy accompanying the change from a gelatinous structure to a granular powder (p. 22).

Simon and Fischer[30] ran the dehydration isobars (1) for the highly gelatinous precipitate thrown down with ammonia and (2) for the less hydrous product obtained by the slow hydrolysis of zirconium tetrachloride in a dialyzer.   From these curves, which are reproduced in Fig. 46, it is apparent that the gelatinous oxide commonly called orthozirconic acid contains no definite hydrates.   This confirms van Bemmelen's[31] conclusions from similar observations made a quarter of a century earlier.   Magnetic susceptibility measurements on the precipitated oxide at various degrees of dehydration likewise indicate that it consists of ZrO_2 with adsorbed water.[32]

Ruer[33] prepared an aged hydrous zirconia by boiling down repeatedly a solution of zirconium oxychloride.   The sol obtained by this process was precipitated by hydrochloric acid, giving what Ruer called a metachloride.   After centrifuging out the precipitate, it was peptized in water and thrown down again with ammonia.   The hydrous

[28] Van Bemmelen: Z. anorg. Chem., **45**, 83 (1905).
[29] Kolloid-Z., **11**, 241 (1912).
[30] Z. anorg. Chem., **185**, 130 (1929).
[31] Z. anorg. Chem., **49**, 125 (1906).
[32] Bourion and Hun: Compt. rend., **187**, 886 (1928).
[33] Z. anorg. Chem., **43**, 297 (1905).

oxide, still containing considerable chloride, was dried over caustic alkali and then heated to 100°, where its water content corresponded approximately to $ZrO_2 \cdot 2/3H_2O$.   On account of its relatively slight solubility in acids and its failure to glow on heating, Ruer believed it to be an isomeric form of zirconic acid which he designated meta-zirconic acid.   Van Bemmelen found, however, that oxides prepared by Ruer's method lost water continuously without any evidence of the existence of a hydrate.   A composition corresponding to Ruer's 100°
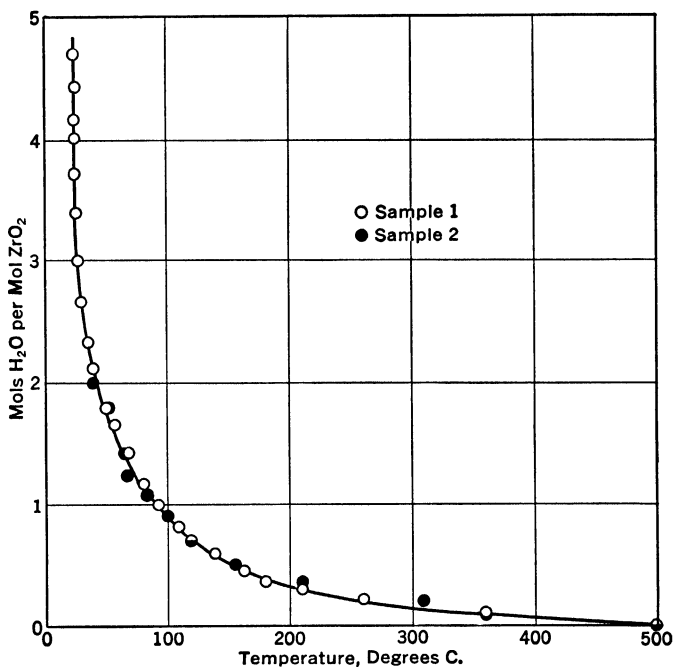
FIG. 46.—Dehydration isobars of hydrous zirconium dioxides.

hydrate was obtained by van Bemmelen at 85°; and at every observed temperature, the composition showed considerable variation with different samples.   Van Bemmelen showed further that Ruer's meta-chloride was merely an aged zirconia with adsorbed chloride.   By evaporating the oxychloride to dryness and replacing the water repeatedly, a product was obtained which retained a trace of chloride. Schmid[34] claimed to get definite crystals of the so-called metazirconic acid by conducting dry ammonia over solid $ZrOCl_2 \cdot 4H_2O$, but it is

[34] Z. anorg. Chem., **167**, 369 (1927).

almost certain that the moist, plastic product which he believed to be crystalline was a pseudomorphic gel after $ZrOCl_2$.

Prolonged boiling of hydrous zirconia in a medium possessing a slight solvent action gives a dense structure that not only is less reactive chemically but also has a much lower adsorption capacity than the gelatinous precipitated oxide. This change in structure is a gradual process involving the formation of a continuous series of products intermediate between the typical ortho and meta oxides. It is unnecessary to start with zirconium oxychloride to prepare the so-called meta oxide. A sol of the ordinary oxide is aged by boiling, the amorphous particles gradually becoming denser and at the same time tending to orient themselves into crystals.[35] Neither the freshly prepared nor the aged oxide gives a definite x-radiogram.

Adsorption by Hydrous Zirconia

On account of its highly gelatinous character, hydrous zirconia possesses a marked adsorption capacity for many substances.[36] The taking up of iodine and ammonia by the hydrous oxide carefully purified by dialysis does not follow the ordinary adsorption rule. Instead, the amount taken up increases with the concentration of the solutions without approaching a constant value, thus indicating the formation of a solid solution. Colloidal solutions of ferric oxide, molybdenum blue, zirconium, and silver are quickly decolorized by shaking with a paste of hydrous zirconia. The blue starch-iodine sol is taken up, giving a blue zirconia gel which is decolorized by heating and becomes blue again on cooling, just as the original sol. Colloidal Congo red is strongly adsorbed, giving a blue adsorption compound which is converted into a red salt by warming.[37] The last-mentioned phenomenon has been observed in a number of instances by Wedekind and Wilke.[38] Thus, arsenic acid is adsorbed in the cold by hydrous zirconia,[39] but on standing or boiling $Zr(HAsO_4)_2$ is formed. A similar thing was observed with phosphoric acid, but adsorption only takes place with the following acids: arsenious, monochloracetic, hydrochloric, and perchloric. Obviously, the tendency to form salts following adsorption is not a question of the strength of the acids.

Zirconia gel rapidly catalyzes the decomposition of hydrogen per-

[35] Böhm and Niclassen: Z. anorg. Chem., **132**, 6 (1924).

[36] Wedekind and Rheinboldt: Ber., **47**, 2142 (1914).

[37] Cf. Bayliss: Chem. Zentr., II, 1095 (1911).

[38] Kolloid-Z., **34**, 83, 283; **35**, 23 (1924).

[39] Cf. Sen: Z. anorg. Chem., **174**, 75 (1928).

oxide, especially in concentrated solutions, but the removal of hydrogen peroxide by the gel during very short periods of contact with dilute solutions can be represented by the usual adsorption equation. After prolonged contact, the hydrogen peroxide in solution is almost completely decomposed, but large amounts remain in the gel. Not all the peroxide taken up by the gel can be titrated by permanganate in 8% sulphuric acid. This is taken to indicate the formation of a complex peroxide following the initial adsorption. The taking up of a series of fatty acids and of substituted benzoic acids by freshly precipitated zirconia increases with the ionization constant of the acids.[40] This indicates that chemical interaction with the adsorbent follows the initial adsorption process.

The adsorption capacity of hydrous zirconia for certain dyes suggests the use of zirconium salts as mordants.[41] For these purposes the hydrous oxide possesses no properties that are distinctive, and so it finds but limited application. A suspension of the dry oxide has been suggested as a protein precipitant for deproteinizing serum plasma or protein solutions.[42]

ZIRCONIA SOL

Formation

Hydrolysis Methods. Biltz prepared an impure sol by dialysis of a solution of zirconium nitrate for several days. The sol, which was positively charged, was employed in the study of the mutual coagulation process. Sharma and Dhar[43] prepared concentrated but not very pure sols in this way by hydrolyzing zirconium nitrate at the boiling point and dialyzing in the hot. Thus, in a sol containing about 75 g per l the ratio $ZrO_2 : NO_3$ was 6.6, and in one containing about 40 g per l the ratio was 16.2. These sols were highly viscous, the viscosity increasing with the purity of the sol, probably owing to coalescence of particles into chain-like aggregates. Unlike the concentrated titania sols, the surface tension of the zirconia sols is appreciably less than that of water (p. 262). This is probably due to the presence of electrolyte in the latter sols.

Ruer[44] dialyzed solutions of zirconium oxychloride both without heating and after heating for 2 hours. Like Biltz's preparation, the sols were clear in transmitted light but cloudy by reflected light.

[40] Chakravarti and Sen: Z. anorg. Chem., **186**, 357 (1930).

[41] Barnes: J. Soc. Chem. Ind., **15**, 420 (1896); Wengraf: Färber-Ztg., **25**, 277 (1914).

[42] Erdös and Sürü: Biochem. Z., **231**, 6 (1931).

[43] J. Indian Chem. Soc., **9**, 455 (1932).

[44] Z. anorg. Chem., **43**, 282 (1905).

Addition of sodium or ammonium chloride caused precipitation, the amount required being less the more thorough the purification by dialysis. A transparent glass was obtained by evaporation on the water bath. The addition of 10 cc of N H_2SO_4 to 2.5 cc of sol containing 0.015 g ZrO_2 gave a precipitate that dissolved in one-half hour provided the solution was not heated before dialysis; the precipitate from the preheated solutions did not dissolve for approximately 6 hours under similar conditions. This decrease in solubility was the manifestation of growth of primary particles which proceeded quite gradually at ordinary temperature but more rapidly at the boiling point. As we have seen, prolonged heating of the oxychloride gave a slightly hydrous mass, insoluble in either hydrochloric or nitric acid, but readily peptized on washing with water. By dialysis of the so-called metachloride, Ruer obtained a milky-white sol which left, on evaporation, an amorphous white residue instead of a glassy mass. The chlorine content was reduced to 0.026 atom Cl per mol of ZrO_2. On account of the relatively slight adsorption capacity of the particles, the precipitation by electrolytes with univalent anions was readily reversible.

Robinson and Ayers[45] prepared sols by allowing a solution of $ZrOCl_2$ to drop slowly into vigorously boiling water, followed by dialysis at 65 to 75° until small amounts of jelly appeared in the collodion dialysis bags. In one such sol containing 2.5 g ZrO_2 per l, the ratio ZrO_2 : Cl was 9.4. Sols prepared in this way were heated in a steel autoclave to temperatures up to 275°. This treatment decreased the hydration of the particles, as evidenced by the increase in intensity of scattered light and the decrease in viscosity of the heated sols. Moreover, the heating decreased the stability toward electrolytes and decreased the pH value by releasing adsorbed hydrogen ion as a result of agglomeration of particles by further hydrolysis of adsorbed salt.

A very satisfactory sol was prepared by Rosenheim and Hertzmann[46] by the dialysis for a week of a 1.5% solution of zirconium acetate. The colloid was perfectly clear in both transmitted and reflected light and contained but a trace of acetate. Heating on the water bath converted the sol into a clear transparent jelly. It was very sensitive to the action of electrolytes, dilute potassium chloride precipitating it quantitatively.

Peptization Methods. Müller[47] prepared sols both by adding

[45] J. Am. Chem. Soc., **55**, 2288 (1933).

[46] Ber., **40**, 813 (1907).

[47] Z. anorg. Chem., **52**, 316 (1907).

freshly precipitated and washed zirconia to a solution of zirconium nitrate and by adding ammonia drop by drop to the nitrate solution until the precipitate first formed just failed to redissolve. Evaporating the sol to dryness gave a gummy residue that swelled in water and was repeptized. The oftener this process was repeated, the smaller the nitrate content became. The sols were precipitated by low concentrations of electrolytes containing multivalent anions. Zirconium sulfate, like the nitrate, peptizes hydrous zirconia. Hauser[48] showed conclusively that the products of the peptizations are sols and not basic salts, $ZrOSO_4$ and $ZrO(NO_3)_2$, as assumed by Berzelius[49] and Paykull.[50]

Szilard[51] added ammonia to a zirconium nitrate solution and washed the resulting gel thoroughly, using the centrifuge, until complete peptization took place. In this way, a highly purified zirconia sol was obtained which was quite sensitive to the action of electrolytes, carbon dioxide from the air being sufficient to induce coagulation. Szilard[52] also peptized the purified gelatinous oxide with the nitrates of zirconium, thorium, and uranyl, obtaining sols similar to those of Müller.

A zirconia sol is said to form by arcing a heated electrode under water in the presence of gum arabic.[53]

Constitution

Adolf and Pauli[54] attempted to establish the composition of equilibrium solutions of zirconium oxychloride, of varying concentrations up to 0.5 N, by observations of the freezing-point lowering, conductivity, and direction of migration under electrical stress, as well as the hydrogen and chloride ion concentrations, using the hydrogen and calomel electrodes, respectively. The hydrolysis does not change materially with the dilution. The curves for hydrogen ion and the chloride ion concentrations against the concentrations of $ZrOCl_2$ are S-shaped and intersect each other at three points, so that, at very low and again at moderate concentrations, the hydrogen ion concentrations appear to be greater than that of chloride, indicating the presence of complex ions containing zirconium. The osmotic concentration at the higher concentrations is less than the molar concentration of

[48] Z. anorg. Chem., **54**, 208 (1907).
[49] Pogg. Ann., **4**, 117 (1825).
[50] Ber., **6**, 1467 (1873).
[51] J. chim. phys., **5**, 488 (1907).
[52] J. chim. phys., **5**, 636 (1907).
[53] Brown: U. S. Pat. 1,910,212 (1930).
[54] Kolloid-Z., **29**, 173 (1921).

oxychloride and does not greatly exceed it even at the greatest dilutions. By subtracting from the total conductivity, that due to the hydrogen and chloride ions present, the conductivity due to the alleged complex zirconium ions is obtained. This appears to constitute a large part of the total conductivity and to vary with the concentration of oxychloride. These observations are explained by assuming the formation of complex cations and anions such as $[2Zr(OH)_4 \cdot ZrOCl_2 \cdot ZrO]^{++}$ and $[2Zr(OH)_4Cl_2]^{--}$. Migration experiments indicate a migration of zirconium to both anode and cathode, more going to the anode than to the cathode when the hydrogen ion concentration exceeds the chloride ion concentration, and *vice versa.*

It is very difficult to make head or tail of the conglomeration of facts and speculations given in the preceding paragraph. This difficulty increases when we reflect that the conductivity and electrometric measurements of Adolf and Pauli do not give what they assumed them to give. Leaving out any complex ions, there are, in any given solution: undecomposed oxychloride, hydrous zirconium dioxide, hydrogen ions, and chloride ions. The hydrous oxide adsorbs some undecomposed zirconium oxychloride and possibly stabilizes it to a certain degree. It also adsorbs both hydrogen ions and chloride ions in amounts depending on the experimental conditions. The conductivity is due to the unadsorbed ions and to the hydrous oxide particles which have adsorbed ions and which move with a velocity somewhat less than that of the free ions. Thus, the adsorbed ions contribute to the conductance of the solution, but they behave abnormally as regards electrometric measurements. Adsorbed chloride ion gives no test with silver nitrate, and its effect on the calomel electrode will be negligible. To assume that all the hydrogen and chloride ions which do not show up in electrometric measurements exist in complex ions, will necessarily lead to erroneous conclusions. Until we know definitely what Adolf and Pauli's conductivity and electrometric measurements actually mean, it seems idle to speculate as to the real nature of solutions of zirconium oxychloride, whether dialyzed or undialyzed. Adolf and Pauli assume the existence of complex ions in sols where the ratio ZrO_2 to Cl is 3 or 4 to 1. This would seem to be a far-fetched assumption in a sol such as Ruer's, where the ratio is 40 or more to 1.

Stability; Thixotropy

As already pointed out, the sols of zirconia are relatively instable when highly purified especially by hot dialysis, requiring but small

amounts of electrolytes to cause coagulation. Addition of suitable amounts of electrolyte causes the sol to set to a jelly[55] unless the particles have been dehydrated by heating to too high a temperature. The jellies are thixotropic, but the reversible sol-jelly transformation cannot be repeated too often without throwing down a gelatinous precipitate. The agglomeration following the setting causes the gel to synerize, the contraction increasing with the electrolyte concentration, as would be expected (p. 202). A jelly which has been broken up by freezing in liquid air will set to a jelly once more on standing.[56]

HYDROUS ZIRCONIUM PEROXIDE

A hydrous peroxide of zirconium was first obtained by adding ammonia to a solution containing zirconium sulfate and hydrogen peroxide.[57] Such gels contain both dioxide and peroxide; but Bailey[58] added hydrogen peroxide alone to solutions of zirconium salts, obtaining gelatinous precipitates which analyzed approximately for $ZrO_3 \cdot 3H_2O$ when dried over phosphorus pentoxide at ordinary temperatures. Schwarz and Giese[59] claimed to remove the adsorbed water by washing with ammonia and arrived at the formula $ZrO_3 \cdot 2H_2O$, but as we have seen repeatedly, this evidence of hydrate formation is unreliable. The oxide loses oxygen on heating, the composition approaching Zr_2O_5 at 100°. Pissarjewski[60] obtained hydrous ZrO_3 by electrolyzing a sodium chloride solution in which hydrous ZrO_2 was suspended. Irrespective of the method of preparation, the higher oxide behaves as a true peroxide, giving off oxygen on standing and yielding hydrogen peroxide when treated with dilute sulfuric acid. The gelatinous oxide is fairly soluble in alkali, and perzirconates are said to form.

HYDROUS THORIUM DIOXIDE

PRECIPITATED THORIA

The ordinary gelatinous form of thorium dioxide is precipitated by adding ammonia or alkalis to a cold solution of thorium salt.

[55] Schalek and Szegvari: Kolloid-Z., **33**, 326 (1923); Prakash and Dhar: J. Indian Chem. Soc., **7**, 417, 591 (1930); Prakash: **9**, 193 (1932); Kolloid-Z., **60**, 184 (1932).

[56] Prakash: Indian J. Phys., **8**, 231 (1933).

[57] Cleve: Bull. soc. chim. (2) **43**, 57 (1885).

[58] J. Chem. Soc., **49**, 149, 481 (1886); Proc. Roy. Soc. (London) **46**, 74 (1890); cf. Hermann: J. prakt. Chem., **97**, 331 (1866).

[59] Z. anorg. Chem., **176**, 209 (1928).

[60] Z. anorg. Chem., **25**, 378 (1900); **31**, 359 (1902).

The fresh gel is readily soluble in mineral acids and is readily peptized by certain acids and salts. The oxide obtained by igniting thorium nitrate, sulfate, or the hydrous oxide is neither dissolved nor peptized by acids, whereas that obtained by igniting the oxalate under suitable conditions is rendered peptizable by boiling down the acids, provided the temperature of ignition of the oxalate does not exceed 700° and that the oxide thus formed is not heated above 500° for any consider-able time. Ignition at very high temperatures causes sintering so that little or no peptization results even with the strongest acids. The transformation from the easily peptized gel to the non-peptizable granules is a continuous process which does not involve an isomeric change from a so-called ortho to a meta form.[61] Moreover, the solution of the oxide from thorium oxalate in hydrochloric acid does not involve the formation of a metachloride[62] since the chloride content of the alleged compound varies through wide limits and the so-called solution in water is a typical sol.

The freshly formed gel gives no x-ray diffraction pattern,[63] but, by heating it in contact with the mother liquor for some time, broad interference bands of thorium oxide are obtained.[63] X-ray analysis of the oxides formed by ignition of the so-called ortho and meta compounds shows that the crystals of both possess identically the same cubic structure.[64] The magnetic susceptibility of the gel varies linearly with the water content, indicating that it is a hydrous oxide and not a hydrate or hydroxide.[65]

For the action of titania and thoria as dehydration catalysts see Vol. I, p. 227.[66] Kistler, Swann, and Appel[67] found thoria aerogel (p. 223) to be an excellent catalyst for the conversion of aliphatic acids and esters to ketones.

[61] Levi and Reina: Atti accad. Lincei (6) **5**, 174 (1927).

[62] Cleve: Bull. soc. chim. (2) **21**, 115 (1874); Stevens: Z. anorg. Chem., **27**, 41 (1901).

[63] Böhm and Niclassen: Z. anorg. Chem., **132**, 1 (1924); Havestadt and Fricke: **188**, 371 (1930); Hüttig, Magierkiewicz, and Fichmann: Z. physik. Chem., **A141**, 1 (1929).

[64] Levi: Giron, chim. ind. applicata, **7**, 410 (1925).

[65] Bourion and Beau: Compt. rend., **198**, 916 (1934).

[66] Cf., *also*, Hoover and Rideal: J. Am. Chem. Soc., **49**, 104, 116 (1927).

[67] Ind. Eng. Chem., **26**, 388, 1014 (1934).

Formation

Biltz[68] obtained dilute, water-clear, positively charged thoria sols by dialysis of 14% solutions of thorium nitrate. Müller[69] obtained similar sols containing as much as 150 g ThO_2 per 1 by peptizing the freshly precipitated and washed hydrous thoria with thorium nitrate, hydrochloric acid, aluminum chloride, ferric chloride, or uranyl nitrate. Peptization of the gel thrown down by ammonia from thorium nitrate solution can be accomplished by thorough washing[70] without the addition of a peptizing electrolyte, provided the washing is done promptly before the gel has aged. Müller's concentrated sols were slightly cloudy but they could be boiled without precipitating. Evaporation to dryness gave a glistening, brittle, varnish-like residue which swelled in water and finally was dispersed into a distinctly opalescent sol.

Nabar, Patel, and Desai[71] showed that non-electrolytes containing hydroxyl groups, such as glycerol and the sugars, prevent the precipitation of hydrous thorium oxide by sodium hydroxide, the protecting action being greater the larger the number of hydroxyl groups in the molecule. The hydrous oxide adsorbs the non-electrolyte, which exerts sufficient peptizing action that this, combined with the preferential adsorption of hydroxyl ion, gives a stable negative sol.

Constitution

Kohlschütter and Frey[72] showed that peptization of the solid oxide by acids is accompanied by a decrease in the volume of the colloidal system which is probably to be explained by the porous nature of the oxide. During peptization, the electrical conductivity and the titer of the acid decrease, and the presence of thorium salts can be proved analytically; but peptization and solution do not proceed parallel to one another.

The positive charge on the sols is due to preferential adsorption of hydrogen and thorium ions. The sol formed with hydrochloric acid contains more or less adsorbed chloride, and chloride is the contra ion. Pauli and Peters[73] believe that the chloride in the micelle is present as $ThO(OH)Cl$, but there is no experimental justification for this

[68] Ber., **35**, 4436 (1902); **37**, 1095 (1904).

[69] Ber., **39**, 2857 (1906); Z. anorg. Chem., **57**, 314 (1908).

[70] Szilard: J. chim. phys., **5**, 488, 636 (1907).

[71] Kolloid-Z., **57**, 173 (1931); cf. J. Indian Chem. Soc., **7**, 162 (1930).

[72] Z. Elektrochem., **22**, 145 (1916).

[73] Z. physik. Chem., **A135**, 1 (1928).

belief. From analytical and potentiometric measurements they deduce the following formula for a specific sol:

$$[138ThO_2 \cdot 2.62ThO(OH)Cl \cdot ThO(OH)]^+ \cdot Cl^-$$

Be this as it may, the adsorbed chloride gives no test with silver nitrate, and free chloride may not be precipitated owing to adsorption of silver chloride by the hydrous oxide which prevents agglomeration into particles large enough to settle.[74]

With thoria sol, as with a number of other sols, Duclaux and Titéica[75] claim that the composition of the ultrafiltrate from the sol is independent of the pressure of ultrafiltration, the concentration of the micelles, the nature of the membrane, and the electromotic force of filtration. In the light of McBain's work (p. 58), these observations appear to be incorrect.

Stability

Pure thoria sols are in general quite sensitive to the action of electrolytes, especially those with multivalent anions. The velocity of coagulation of the sol by electrolytes has been followed by observing the change in the intensity of the light scattering[76] with a photoelectric cell. The equation of Smoluchowski was found to apply up to a limited concentration of the coagulating electrolyte (p. 119). The process of slow coagulation is autocatalytic, as evidenced by the S-shape of the coagulation-time curve. The S-shape gradually disappears, however, as (1) the stabilizing electrolyte is removed by dialysis, (2) the sol is diluted, and (3) the concentration of coagulating electrolyte, that is the rate of coagulation, is increased.

The adsorption of precipitating ions during coagulation of the sol follows the usual rules:[77] (1) the higher the charge on the particles, the greater the adsorption; and (2) the higher the adsorption of the stabilizing ion of an electrolyte, the greater the adsorption of the precipitating ion.[78] Non-electrolytes such as methyl, ethyl, and propyl alcohol cut down the adsorption of sulfate, the lower members of the homologous series being most effective.

[74] *Cf.* Hantzsch and Desch: Ann., **323**, 38 (1902); Ruer: Z. anorg. Chem., **43**, 85 (1905).

[75] Rev. gén. colloïdes, **8**, 251 (1930).

[76] Desai: Trans. Faraday Soc., **24**, 181 (1928); Patel and Desai: **26**, 128 (1930); *cf.* Mehta and Joseph: J. Indian Chem. Soc., **10**, 177 (1933); Karekar and Patel: Trans. Faraday Soc., **30**, 493 (1934).

[77] Karekar and Patel: Kolloid Z., **68**, 286 (1934).

[78] *Cf.* Weiser: J. Phys. Chem., **25**, 665 (1921); **28**, 232 (1924).

Application

The most important application of thoria sol that has yet been suggested is its introduction into the blood stream, the lymphatics, the bladder, and the kidneys in order to render them opaque to x-rays so that clinical examination can be made.[79]   As we have seen, the sol can be made stable in neutral or alkaline media by the addition of colloidal carbohydrates, amyloses, etc.[80]   It is reported that the sol casts a good shadow, and its wide application may be expected if it is found to be harmless.   Unfortunately, the thoria is held so firmly by the reticulo endothelial cells that it is eliminated very slowly. On the other hand, it appears to be non-toxic and shows no radio-activity.

HYDROUS THORIUM PEROXIDE

Thorium peroxide is thrown down in a gelatinous form by adding hydrogen peroxide to a solution of thorium acetate, sulfate, or nitrate.[81]   The gel adsorbs acids quite strongly; hence, it is very difficult to obtain in a pure state.[82]   Wyrouboff and Verneuil attempted to avoid contamination by carrying out the precipitation in the presence of an excess of ammonia, but under these conditions, the precipitate contained nitric acid resulting from the action of hydrogen peroxide on the ammonia.   The peroxide is formed by the action of hydrogen peroxide on hydrous thorium dioxide and also by electrolysis of a sodium chloride solution in which the dioxide is suspended.   The latter method of formation indicates that the product is a true peroxide and not an addition compound of hydrous thorium dioxide and hydrogen peroxide.

The freshly prepared peroxide appears to be hydrous Th_2O_7, but this is quite instable, going over on standing to the much stabler ThO_3.[83]   In this case also, Schwarz and Giese claim that the oxide gives a hydrate, but the evidence is not conclusive.   Dilute sulfuric acid reacts with it, giving hydrogen peroxide, and strong sulfuric acid gives ozone.   Unlike the corresponding compounds of titanium and zirconium, it is not attacked by alkalis.

[79] Gottlieb: Can. Med. Assoc. J., **27**, 356 (1932); Sorge: Boll. soc. ital. biol. sper., **7**, 1215 (1932); Någeli and Lauche: Klin. Wochschr., **11**, 2029 (1932).

[80] Heyden: French Pat. 740,229; British Pat. 379,133 (1931).

[81] Wyrouboff and Verneuil: Ann. chim. phys. (8) **6**, 441 (1905).

[82] Lecoq de Boisbaudran: Compt. rend., **100**, 605 (1885); Cleve: Bull. soc. chim. (2) **43**, 53 (1885).

[83] Pissarjewski: Z. anorg. Chem., **31**, 359 (1902); **25**, 378 (1900).

CHAPTER X

THE HYDROUS OXIDES OF THE RARE EARTHS

The term rare earths is applied to a group of closely related trivalent metals forming basic oxides with oxalates insoluble in dilute mineral acids. The rare-earth group includes scandium, yttrium, and lanthanum, together with all the elements between cerium, atomic number 58, and lutecium, atomic number 71, inclusive. These elements are frequently divided into three families, the basis for the arbitrary classification being the solubility of the double alkali sulfates.[1] The elements of the cerium family, scandium, lanthanum, cerium, praseodymium, neodymium, and samarium, form quite insoluble double sulfates; and the elements of the yttrium family, dysprosium, holmium, erbium, thulium, yttrium, ytterbium, and lutecium, form quite soluble double sulfates. On the border line between these two families are the terbium family elements: europium, gadolinium, and terbium, whose double sulfates are but moderately soluble. The hydrous oxides of the cerium group are the best known and will be considered separately, beginning with hydrous ceric oxide.

HYDROUS CERIC OXIDE

PRECIPITATED CERIC OXIDE

Cerium differs from all the other members of the rare-earth family in forming a definite series of ceric salts derived from the most stable oxide of cerium, CeO_2. It is only as a trivalent metal that cerium exhibits the properties of a typical rare earth.

Hydrous ceric oxide is precipitated as a yellowish, highly gelatinous mass by adding ammonia or alkali to a solution of ceric salt. It is also formed by oxidizing hydrous cerous oxide suspended in water, either by the oxygen of the air or by adding an oxidizing agent such as chlorine, bromine, alkali hypochlorite, or sodium peroxide. Like most gelatinous precipitates, it adsorbs alkali salts and hydroxide

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[1] Urbain: Ann. chim. phys. (7) **19,** 184 (1900).

strongly and so is best obtained pure by precipitating cold ceric ammonium nitrate with ammonia, allowing the washed precipitate to dry partially, and finally rewashing to remove all ammonium nitrate. The precipitate has been dried to compositions corresponding to hydrates,[2] but a 21° isotherm obtained by Desai[3] indicates that the precipitates form no hydrates. Moreover, Böhm and Niclassen[4] found that the gels precipitated at temperatures as low as 0° gave the same x-ray diffraction patterns as anhydrous CeO_2. X-ray analysis of the oxide indicates a face-centered, cubic crystalline structure of the CaF_2 type.[5] The gel loses a large part of its adsorbed water on standing and is transformed into a fibrous or granular mass. If dried below 120° it dissolves in both acids and alkalis, but the ignited oxide is quite insoluble.[6]

Although the highly dispersed gelatinous oxide free from praseodymium[7] is white,[8] it assumes a citron-yellow color when calcined at a high temperature, becoming white or a lighter yellow again on cooling. The tint assumed on ignition depends on the mode of preparation: that obtained by igniting the hydrous oxide is darker than that from the sulfate, but according to Wyrouboff and Verneuil,[9] the tint of neither is definite enough to be described other than as a shade of white. Spencer[10] attributes the yellow color to polymerization, and Sterba[11] suggests that it may be due to a higher oxide. There seems to be no experimental justification for either of these assumptions, and the author is inclined to believe that the color assumed on heating is due to coalescence of particles which appear white in a finer state of subdivision. It is well known that zinc oxide is yellow when hot, because of coalescence of particles, but disintegration takes place on cooling, accompanied by a return to the white color. However, a thoroughly sintered mass of zinc oxide

[2] Wyrouboff and Verneuil: Ann. chim. phys. (8) **9**, 289 (1906); Rammelsberg: Pogg. Ann., **108**, 40 (1859); Erk: Z. Chem. (2) **7**, 100 (1871); Carnelley and Walker: J. Chem. Soc., **53**, 59 (1888).

[3] Kolloid-Beihefte, **26**, 422 (1928).

[4] Z. anorg. Chem., **132**, 1 (1924).

[5] Goldschmidt, Ulrich, and Barth: Skrifter Norske Videnskaps-Akad. Oslo, I, **5**, 5 (1925); Davey: Phys. Rev. (2) **23**, 763 (1924); Böhm: Z. anorg. Chem., **149**, 217 (1925).

[6] Mengel: Z. anorg. Chem., **19**, 71 (1899).

[7] Witt: Chem. Ind., **19**, 156 (1896).

[8] Cf., *however*, Brauner: Z. anorg. Chem., **34**, 207 (1903).

[9] Ann. chim. phys. (8) **9**, 356 (1906).

[10] J. Chem. Soc., **107**, 1272 (1915); Meyer: Z. anorg. Chem., **37**, 378 (1903).

[11] Compt. rend., **133**, 221 (1901); Ann. chim. phys. (8) **2**, 193 (1904).

remains yellow indefinitely, even on cooling.[12]   Similarly, the citron-yellow color of hot ceric oxide becomes white or light yellow on cooling, depending on the time and temperature of ignition.   The oxide has been suggested as a yellow opacifying agent for glass and enamel.[13]

Cerium salts may be used more or less successfully for tanning leather[14] and as a mordant in dyeing cotton.[15]   In both these processes, the hydrous oxide plays an important rôle.

The precipitate of hydrous ceric oxide obtained in the cold by adding sodium peroxide to a solution of cerous salt is reddish brown in color, but on boiling, oxygen is evolved and the color disappears.[6] The red-brown color may be due to a higher oxide of cerium, possibly hydrous CeO_3,[16] which is instable at 100°.

<div align="center">CERIC OXIDE SOL</div>

Formation

Ceric oxide sol is best prepared by dialysis of a solution of ceric ammonium nitrate.[17]   The resulting sol may be evaporated to dryness on the water bath, giving a gummy mass which goes into colloidal solution again on shaking with water.   The sol may be prepared also by peptization of the precipitated oxide with hydrochloric acid,[18] but an excess of peptizing agent is required.

Like hydrous chromic oxide and ferric arsenate, the sol prepared by dialysis of ceric ammonium nitrate sets to a firm jelly if the dialysis is carried too far.[19]   This is particularly noticeable if the initial con-centration of the peptizing agent, nitric acid, falls below a critical value that is determined in part by the presence in the sol of ammonium nitrate.[20]   Thus a jelly returns to the sol condition if shaken up with a quantity of fresh undialyzed sol, and the concentration of

[12] Farnau: J. Phys. Chem., **17**, 653 (1913).

[13] Rickman and Rappe: German Pat. 203,773 (1907).

[14] Eitner: Gerber, **37**, 199, 213 (1911); Garelli: Collegium, 418 (1912); Parenzo: 121 (1910).

[15] Matschak: Chem. Ind., **21**, 150 (1898); Witt: **19**, 156 (1896); Waegner and Müller: Z. Farben-u. Textil Chem., **2**, 290 (1903); Baskerville and Foust: J. Soc. Chem. Ind., **23**, 104 (1904).

[16] Lecoq de Boisbaudran: Compt. rend., **100**, 605 (1885); Cleve: Bull. soc. chim. (2) **43**, 53 (1885); Knorre: Z. angew. Chem., **11**, 687, 717 (1897); Schwarz and Giese: Z. anorg. Chem., **176**, 209 (1928).

[17] Biltz: Ber., **35**, 4431 (1902); Z. anorg. Chem., **168**, 96 (1927).

[18] Kruyt and van der Made: Rec. trav. chim., **42**, 277 (1923).

[19] Fernau and Pauli: Kolloid-Z., **20**, 20 (1917).

[20] *Cf.* Kruyt and van der Made: Rec. trav. chim., **42**, 277 (1923).

electrolyte necessary to precipitate the hydrous oxide as a jelly is increased by adding a small amount of nitric acid.

Aging

.Like the precipitated oxide, the primary particles in the sol coalesce and lose water more rapidly than is usual with sols of the hydrous oxides. This aging is readily followed viscosimetrically, since the loss of adsorbed water by the dispersed particles is accompanied by a marked decrease in viscosity. In Fig. 47 is given the curve obtained by Kruyt and van der Made[18] for a sol containing 1.28 g CeO_2 per l which was prepared by dialysis of a 6% ceric ammonium nitrate solution short of the appearance of any jelly on the membrane (30 hours). The initial increase in viscosity is a manifestation of gelation; with a relatively strong sol, this may proceed to the point
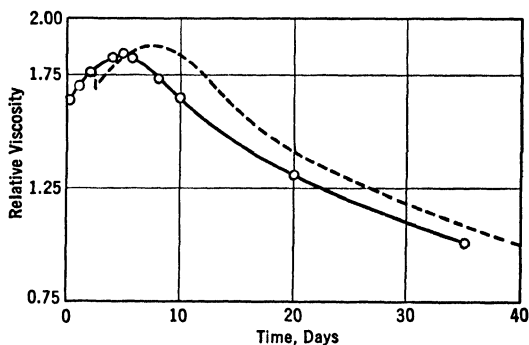
FIG. 47.—Change in viscosity of CeO_2 sols with time.

where the time of flow can no longer be measured, followed in the course of a few weeks by a decrease in viscosity until the value of an aged sol is reached. If gelation has already started in the dialyzer before the viscosity measurements are begun, the maximum in the viscosity curve is missed. Nor is it observed after the sol has been heated to 50°, which causes rapid aging, or when the concentration of the sol is too low to admit of marked coalescence of the hydrous particles. Thus, the character of a hydrous ceric oxide sol is influenced to a marked degree by relatively slight variations in the method of dialysis, concentration, temperature, and time.[19] The particles of a heated sol or one aged by long standing in the cold are no longer sufficiently hydrous to give a jelly on precipitation, at least in concentrations as low as 1.5% CeO_2.

Action of Electrolytes and Radiations—Jellies

Kruyt and van der Made added to a fresh sol insufficient salt to produce coagulation and observed an immediate drop in the viscosity of the sol, followed by a gradual increase in viscosity, the final product

being a jelly; with still less salt the initial diminution in viscosity was followed by an increase to a maximum and thereafter by a slow decrease as indicated by the dotted curve in Fig. 47.

β- and γ-rays from radium[21] and x-rays[22] act on the sol in much the same manner as electrolytes. Prolonged action produces a firm, stable jelly, whereas shorter action results in a viscosity-time curve readily distinguished from the electrolyte curve by a much steeper rise and fall on opposite sides of the maximum, as shown by the results of observations of Fernau and Pauli represented in Fig. 48.
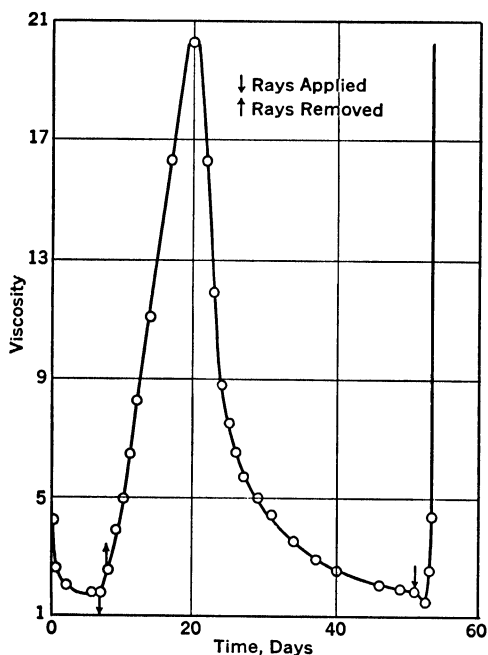
FIG. 48.—Effect of β-rays from radium on the viscosity of CeO_2 sol.

The sols used in these experiments contained 0.96% CeO_2 and had already begun to decrease in viscosity when the measurements were started. On the seventh day the sol was subjected, for 13 hours only, to the action of β-rays from radium. This brought about a sharp rise in viscosity, which reached a maximum on the twentieth day, followed by a sharp fall. On the fifty-first day the β-rays were applied continuously until gelation took place on the fifty-fifth day.

Crowther compared the action of x-rays and β-rays on the same ceric oxide sol. Comparable results for the two types of radiation are shown graphically in Fig. 49. It is apparent that a numerical equivalence exists between the action of x-rays and that of β-particles so far as discharge of the colloidal particles is concerned. From the curves, the agglomerating power of the x-rays would appear to be greater than that of β-rays. This is not necessarily the case, however,

[21] Fernau and Pauli: Kolloid-Z., **20**, 20 (1917); Crowther: Phil. Mag. (7) **7**, 86 (1929).

[22] Fairbrother: Phil. Mag. (7) **6**, 385 (1928).

since the conditions under which the two types of radiation are applied differ so widely that it is impossible to compare the agglomerating action directly.

Under the influence of a suitable amount of electrolytes or prolonged action of radiations, the charge on the particles is neutralized. This is apparently accompanied by a loss of adsorbed water and a consequent lowering of the viscosity, gradually under the influence of β- and γ-rays but immediately when an electrolyte is added. The subsequent increase in viscosity is due to aggregation of the electrically neutral particles forming a jelly. The attainment of a maximum viscosity and the subsequent fall, when the added electrolyte is small in amount or the time of exposure to the rays is comparatively brief, is attributed by Fernau and Pauli to the peptizing action of electrically charged particles entangled in the jelly. Since hydrogen ion is the stabilizing ion of the sol, observations of the changes in the hydrogen

FIG. 49.—Change in viscosity of CeO_2 sol with varying exposure to x-rays and β-rays.

ion concentration might throw some light on the anomalous behavior during the aging process.

Kruyt and van der Made studied the effect of different electrolytes on the nature of the precipitate, obtaining stable jellies that do not contract in some instances and undergo rapid syneresis or form a gelatinous precipitate in others. From what has been said (p. 202), this is a question of the amount of electrolyte added to effect coagulation. Jellies with similar properties should result if the concentrations of electrolytes necessary for a suitable rate of coagulation do not differ widely. If the rate of coagulation is too high, gelatinous precipitates or imperfect jellies will form; if electrolytes with univalent anions are employed, the high concentration necessary for agglomeration will favor marked syneresis (p. 203). The order of concentration of ions

necessary for jelly formation in 24 hours is: $Br > ClO_4 > Cl > NO_3$ $> CNS > I > SO_4 > HPO_4$. Alcohol likewise decreases the stability of the sol toward electrolytes and, in concentrations of 40 to 50%, precipitate it as a jelly; sugars, on the other hand, stabilize the sol.[23]

The rate of the coagulation of the sol by electrolytes has been followed spectrophotometrically by Nabar and Prasad.[24]   The coagulation-velocity curves are S-shaped as with thoria sols (p. 274).

OTHER HYDROUS OXIDES OF THE CERIUM FAMILY

Hydrous Cerous Oxide. This compound is obtained as a pure white[25] gelatinous precipitate by treating a cerous salt solution with ammonia or alkali in the absence of air.   It oxidizes readily in the air, especially in the presence of alkali,[26] the color changing to violet and finally to light yellow, owing to the formation of hydrous CeO_2.   A similar color is obtained by heating ceric carbonate, nitrate, oxalate, or oxide, in hydrogen.   Since one would not expect a mixture of two light bodies to be violet, the colored body is probably a cero-ceric oxide to which Chase[27] and Meyer[28] assign the formula Ce_4O_7 or $2CeO_2 \cdot Ce_2O_3$; and Wyrouboff and Verneuil,[29] the formula Ce_7O_{12} or $3CeO_2 \cdot 2Ce_2O_3$.   The latter investigators obtained the violet product directly by adding alkali to a mixed solution of cerous and ceric salts, the maximum intensity resulting when the ratio of cerous to ceric ion was 2 to 1.

Hydrous Praseodymium Oxide. The gelatinous mass of hydrous Pr_2O_3, precipitated from a praseodymium salt by alkalis, is bright green in color and can be dried to a green powder which has, probably erroneously, been assumed to be a trihydrate.[30]   If the hydrous oxide, the oxalate, or the nitrate of praseodymium is heated in air, a black powder is obtained, intermediate in composition between Pr_2O_3 and PrO_2;[31] but the exact composition depends on the substance calcined and the temperature of calcination.[32]   In the presence of a

[23] Prasad and Nabar: J. Indian Chem. Soc., **9**, 609 (1932); **10**, 53 (1933).

[24] J. Indian Chem. Soc., **10**, 153 (1933).

[25] Dennis and Magee: J. Am. Chem. Soc., **16**, 649 (1894); Damiens: Ann. chim. (9) **10**, 137 (1918).

[26] Spencer: J. Chem. Soc., **107**, 1265 (1915).

[27] J. Am. Chem. Soc., **39**, 1576 (1917).

[28] Z. anorg. Chem., **37**, 378 (1903); cf. Sterba: Ann. chim. phys. (8) **2**, 193 (1904).

[29] Ann. chim. phys. (8) **9**, 289 (1906); Compt. rend., **128**, 501 (1899).

[30] Cf. Damiens: Ann. chim. (9) **10**, 181 (1918).

[31] Welsbach: Monatsh., **6**, 477 (1885); Jones: Am. Chem. J., **20**, 345 (1898); Schottländer: Ber., **25**, 569 (1892); Meyer: Z. anorg. Chem., **41**, 97 (1904).

[32] Schéele: Ber., **32**, 409 (1899).

small amount of CeO_2, which appears to act as an oxygen carrier, the product approaches near the limit PrO_2.[33] It may be that products of intermediate composition are not definite chemical individuals but are mixtures representing intermediate stages in the oxidation of the lower oxide. In the present state of our knowledge, it is, of course, open to anyone to postulate an intermediate oxide, such as seems necessary to account for the color changes accompanying the oxidation of Ce_2O_3. Prandtl and Huttner claim that the formula of the intermediate product is Pr_6O_{11}. Brauner[34] claims to get $Pr_2O_5 \cdot xH_2O$ by adding hydrogen peroxide to a praseodymium salt before precipitating.

Hydrous Scandium Oxide. Alkalis and ammonia precipitate hydrous Sc_2O_3 as a white voluminous mass, insoluble in excess of precipitant. Like hydrous alumina, the freshly formed oxide glows on heating,[35] but it loses the property on standing since it goes over to a definitely crystalline oxide. By dialysis of a solution of $ScCl_3$ to which ammonia is added short of precipitation a sol results which sets to a thixotropic jelly when treated with a suitable amount of electrolyte.[36]

Hydrous Lanthanum Hydroxide. The voluminous white precipitate formed by adding ammonia to a solution of lanthanum salt, or by adding water to La_2O_3, is hydrous $La_2O_3 \cdot 3H_2O$ or $La(OH)_3$. It gives a definite x-ray diffraction pattern[37] which is different from that of the anhydrous oxide.[38] From the dehydration isobar of the hydroxide, Hüttig and Kantor conclude that a monohydrate forms as in the dehydration of $Al_2O_3 \cdot 3H_2O$. The evidence is not conclusive, however, since the alleged monohydrate gives no characteristic x-ray diffraction pattern such as one would expect if a definite hydrate were formed.

The basic reaction of lanthanum hydroxide is comparable to that of ammonia;[39] hence, the gelatinous oxide absorbs carbon dioxide from the air, and even the ignited oxide is readily soluble in acids. The basicity

[33] Jäger: Proc. Acad. Sci. Amsterdam, **16**, 1095 (1914); Marc: Ber., **35**, 2382 (1902); Prandtl and Huttner: Z. anorg. Chem., **149**, 235 (1925).

[34] Proc. Chem. Soc., **17**, 66 (1901); cf. Melikov and Klimenko: J. Russ. Phys.-Chem. Soc., **33**, 663, 739 (1901).

[35] Böhm: Z. anorg. Chem., **149**, 217 (1925).

[36] Böhm and Niclassen: Z. anorg. Chem., **132**, 6 (1923); Schalek and Szegvari: Kolloid-Z., **33**, 326 (1923).

[37] Hüttig and Kantor: Z. anorg. Chem., **202**, 421 (1931).

[38] Zachariasen: Z. physik. Chem., **123**, 134 (1926); Z. Krist., **70**, 187 (1929); Pauling: **69**, 415 (1928).

[39] Vesterberg: Z. anorg. Chem., **94**, 371 (1916).

of the oxide would seem to preclude the formation of lanthanates, although Baskerville and Catlett[40] claim to have prepared complex compounds of this type by fusing lanthana with potassium hydroxide or by digesting the oxide with strong solutions of alkali. Undoubtedly, the products were hydrous lanthanum hydroxide with adsorbed alkali.[41]

A transparent sol is obtained by peptizing the freshly formed hydrous hydrate with a small amount of dilute hydrochloric acid.[42]

Hydrous Neodymium Oxide. The gelatinous oxide precipitated from a highly purified solution of a neodymium salt is blue and gives blue Nd_2O_3 on ignition. The blue color may be modified by the presence of impurities. By heating neodymium oxalate to a red heat in a stream of oxygen, Waegner[43] obtained a rose-colored product which gave a distinctly different reflection spectrum from Nd_2O_3 and which appeared to be a higher oxide of the formula Nd_4O_7. By suitable choice of conditions, mixed spectra of Nd_2O_3 and the so-called Nd_4O_7 were obtained. Similar observations were made on heating the hydrous oxide and the anhydrous nitrate and carbonate. Joye and Garnier[44] claim that the different-colored products are not due to the oxygen content but to the degree of hydration of Nd_2O_3. Thus the hydrous oxide dried in air was taken to be $Nd(OH)_3$; on heating this to 320°, it has a formula corresponding to $Nd_2O_3 \cdot 1.5H_2O$ and gives a reflection spectrum corresponding to that of a similarly colored oxide described by Waegner; on further heating to 520°, the oxide has the composition $Nd_2O_3 \cdot H_2O$ and gives a reflection spectrum identical with Waegner's Nd_2O_7. These data are interpreted to establish the existence of three hydrates of Nd_2O_3 and the non-existence of a higher oxide, but they are not conclusive. Thus, Garnier claims to get the same reflection spectrum by heating the hydrous oxide that Waegner does by heating what he says is an anhydrous salt, thereby precluding the formation of a hydrate. Of course, it may be argued that Waegner's salts decomposed during dehydration, but this cannot be true, at least of the carbonate which gives up all its hydrate water below 200°[45] and does not start to decompose until above 300°. Moreover, the view that the rose-colored product is a hydrate does not

[40] J. Am. Chem. Soc., **26**, 75 (1904).

[41] *Cf.* Zambonini and Carobbi: Gazz. chim. ital., **54**, 46, 53 (1924).

[42] Böhm and Niclassen: Z. anorg. Chem., **132**, 6 (1924).

[43] Z. anorg. Chem., **42**, 118 (1904).

[44] Compt. rend., **154**, 510 (1912); Garnier: Arch. sci. phys. nat. (6) **40**, 93, 199 (1915).

[45] Preiss and Rainer: Z. anorg. Chem., **131**, 287 (1923).

fit in with Waegner's observation that gentle heating in a current of hydrogen converts it into clear-blue Nd_2O_3. Obviously the whole problem should be reinvestigated.

The blue gelatinous precipitate of the hydrous oxide is readily peptized by dilute hydrochloric acid, forming a beautiful blue sol.[42]

Hydrous Samarium Oxide. Gelatinous samarium oxide is almost white with a pale yellow tinge which is not appreciably intensified on ignition to Sa_2O_3. According to Cleve,[46] if the precipitation with ammonia is carried out in the presence of hydrogen peroxide, a hydrous oxide of the formula $Sa_4O_9 \cdot xH_2O$ results which is similar in appearance to hydrous Sa_2O_3.

THE HYDROUS OXIDES OF THE TERBIUM FAMILY

The hydrous oxides of europium, gadolinium, and terbium are obtained in the same way as the corresponding compounds of the cerium family, by the action of alkali or ammonia on solutions of their salts. When freshly prepared, the gelatinous oxides rapidly absorb carbon dioxide when exposed to the air. Anhydrous Gd_2O_3 and Tb_2O_3 are white solids, whereas Eu_2O_3 possesses a reddish yellow tinge.[47] All the oxides are soluble in acids; but Gd_2O_3 dissolves very slowly at the start, the velocity increasing as the action proceeds.[48] When terbium oxalate is ignited, it gives a dark brown peroxide which approaches the composition required for TbO_2. If a mixture of air and coal gas is passed over TbO_2 or a mixture of Gd_2O_3 and TbO_2 is heated almost to redness, the whole mass immediately becomes incandescent and the gas often takes fire.[49]

THE HYDROUS OXIDES OF THE YTTRIUM FAMILY

Dysprosium, holmium, erbium, thulium, yttrium, ytterbium, and lutecium all form highly gelatinous oxides when thrown down from their salt solutions with ammonia. Like hydrous alumina, the gels of Er_2O_3 and Y_2O_3 become microcrystalline on standing,[4] and it is probable that the other oxides behave similarly. Hydrous Ho_2O_3 has a pale yellow color; Er_2O_3 is rose red; Tm_2O_3 is white with a greenish tinge; and Dy_2O_3, Y_2O_3, Yb_2O_3, and Lu_2O_3 are white. Hydrous peroxides of yttrium, $Y_4O_9 \cdot xH_2O$, and of erbium,

[46] Bull. soc. chim. (2) **43**, 53 (1885).
[47] Prandtl: Ber., **55B**, 692 (1922).
[48] Benedicks: Z. anorg. Chem., **22**, 393 (1900).
[49] Bissel and James: J. Am. Chem. Soc., **38**, 873 (1916).

$ErO_2 \cdot xH_2O$, are formed by adding hydrogen peroxide and ammonia to solutions of their respective salts.[50]

On account of the gelatinous character of the precipitated oxides, it is probable that all of them will form sols, but so far, only two have been described. Böhm and Niclassen[42] dialyzed a solution of erbium nitrate to which ammonia was added short of precipitation. This sol set to a jelly on the addition of a suitable amount of precipitating electrolyte. Müller[51] peptized the hydrous oxide of yttrium with dilute hydrochloric acid, aluminum chloride, and ferric chloride; Szilard[52] employed thorium acetate. McCutcheon and Smith[53] prepared sols of Y_2O_3 and Al_2O_3 by electrolysis of the respective chlorides with a mercury cathode and a rotating silver anode.

[50] Cleve: Bull. soc. chim. (2) 21, 196 (1874).
[51] Z. anorg. Chem., 57, 314 (1908).
[52] J. chim. phys. 5, 488, 636 (1907).
[53] J. Am. Chem. Soc., 29, 460 (1907).

CHAPTER XI

THE HYDROUS OXIDES OF THE FIFTH GROUP

The elements of the fifth group which form hydrous oxides are vanadium, columbium, tantalum, antimony, and bismuth. These will be taken up in the order named.

HYDROUS VANADIUM PENTOXIDE

PRECIPITATED VANADIUM PENTOXIDE

The addition of a mineral acid to a concentrated solution of an alkali or alkaline earth vanadate throws down vanadium pentoxide as a red-brown amorphous, hydrous mass, closely resembling hydrous ferric oxide. A similar precipitate results from the hydrolysis of vanadium oxychloride.[1] The gel is made up of very fine particles which cannot be washed free from the mother liquor without undergoing peptization. By drying in the air, von Hauer[2] realized a composition approaching that of a dihydrate which was taken to be pyrovanadic acid, $H_4V_2O_7$, analogous to the corresponding phosphorus compound. Continuing the drying over sulfuric acid until another molecule of water is lost gives the correct formula for metavanadic acid, HVO_3.[3] The exact investigations of Düllberg[4] show, however, that the red-brown gel is not an acid but is hydrous vanadium pentoxide whose water content depends on the conditions of drying. This has been confirmed by Hüttig and König[5] for the gel which separates slowly at room temperature when ammonium vanadate is treated with nitric acid and allowed to stand quietly. If the mixture is shaken vigorously during the separation of the oxide over a period of 50 hours, the dehydration curve shows a break corresponding to a hemihydrate, $V_2O_5 \cdot 0.5H_2O$ or $H_2V_4O_{11}$. A similar type of curve is

[1] Moissan: Bull. soc. chim. (3) 15, 1278 (1896).

[2] J. prakt. Chem., 80, 324 (1860).

[3] Fritzsche: J. prakt. Chem., 53, 93 (1851); Manasse: Ann., 240, 23 (1887).

[4] Z. physik. Chem., 45, 129 (1903).

[5] Z. anorg. Chem., 193, 81 (1930); Hüttig and Toischer: Kolloid-Beihefte, 31, 347 (1930).

obtained for the product which results on heating the gel for 40 hours at 100° in a bomb tube. The x-ray diffraction pattern of the alleged hemihydrate consists of two definite lines in a position near to but apparently not identical with two lines in the x-radiogram of anhydrous V_2O_5.

If the vanadate-nitric acid mixture is shaken at daily intervals instead of being allowed to stand quietly, the resulting precipitate gives a dehydration isobar with two steps, one corresponding to the monohydrate $V_2O_5 \cdot H_2O$ or HVO_3 metavanadic acid, and the other to the hemihydrate. The x-ray diffraction pattern of the monohydrate is entirely different from that of the anhydrous oxide.

Since the conditions for transforming the hydrous oxide into the monohydrate are not as clearly defined as they should be, and since the existence of the hemihydrate is not established beyond question, the observations of Hüttig should be confirmed and extended.

VANADIUM PENTOXIDE SOL

FORMATION

Biltz[6] treated ammonium vanadate with a dilute solution of hydrochloric acid, obtaining vanadium pentoxide as a brownish red powder. After thorough washing to remove excess electrolyte, the oxide peptizes completely in water, giving a clear reddish yellow sol. The colloidal particles are negatively charged and are highly hydrous. Addition of ammonium chloride to a concentrated sol causes it to set to a jelly; and a dilute sol is precipitated as reddish yellow, highly gelatinous flocs that settle very slowly. If the washed oxide is dried before being peptized, the particles in the sol are larger and are precipitated in less voluminous flocs which settle more rapidly. Wegelin[7] precipitated vanadium pentoxide completely by hydrolysis of a boiling solution of vanadium oxychloride. This is peptized by washing, but the particles are larger and less hydrous than those in the Biltz sol. When treated with electrolytes, the particles agglomerate into dense clumps that settle out rapidly. The precipitate from a boiled Biltz sol is likewise much denser and darker than from an unboiled sol.[8]

Müller[9] obtained a sol by triturating the granular mass produced

[6] Ber., **37**, 1098 (1904).

[7] Kolloid-Z., **11**, 25 (1912).

[8] Freundlich and Leonhardt: Kolloid-Beihefte, **7**, 193 (1915).

[9] Kolloid-Z., **8**, 302 (1911); *cf.* Wegelin: Kolloid-Z., **14**, 65 (1914).

by sudden cooling of molten vanadium pentoxide either by plunging the containing vessel of platinum into cold water or by pouring the melt into cold water. Sols formed in this way are reddish brown in color. The precipitation by ammonium chloride is reversible; but the dense brown residue obtained by evaporating the sol to dryness on the water bath is not repeptized by water, whereas the looser yellow mass resulting from evaporation of the Biltz sol is easily repeptized.

Freundlich and Leonhardt[10] peptized an amorphous, ocher-yellow oxide obtained by gentle ignition of ammonium vanadate. This takes up water from air saturated with moisture, the color becoming reddish yellow. The sol formed by triturating with a little water, followed by shaking with an excess of water, is orange yellow in color; but on standing for several days with occasional shaking, it changes to a yellowish red.

The esters of orthovanadic acid are readily hydrolyzed by water, and Prandtl and Hess[11] took advantage of this reaction to prepare "electrolyte-free" vanadium pentoxide sols. For this purpose, the tertiary butyl ester is particularly satisfactory, both because it is a stable salt and because the hydrolysis product, tertiary butyl alcohol, can be removed from the sol almost completely by boiling. The sols are orange when first prepared, but are changed to yellowish red by heating.

COMPOSITION

Vanadium pentoxide sols always contain a small amount of the oxide in molecular solution. This portion, yellow in color, passes through a dialyzing membrane and is not thrown down by electrolytes. Since the sol is slightly acid, the yellow solution is a vanadic acid or a mixture of vanadic acids. Düllberg claims that only the hexavanadic acid, $H_4V_6O_{17}$, exists in solution, but Jander and Jahr[12] conclude from electrometric titration data that mono-, di-, tetra-, and pentavanadic acids are formed, successively, by increasing the pH value of an alkali vanadate solution, and that pentavanadic acid is identical with the acid commonly designated as hexavanadic. In any event, the complex vanadate anion is strongly adsorbed by the hydrous oxide and gives to the colloidal particles a negative charge. In the

[10] Kolloid-Beihefte, **7**, 187 (1915); *cf.* Ditte: Compt. rend., **101**, 699 (1885).

[11] Z. anorg. Chem., **82**, 116 (1913); *cf.* Riedel: Chem. Zentr., I, 1738 (1914).

[12] Z. anorg. Chem., **212**, 1 (1933); *cf., however*, Britton and Robinson: J. Chem. Soc., 1261 (1930); 1955 (1932).

Biltz sol the contra ions are both hydrogen ion and ammonium ion derived from the salt used in its preparation.[13]

The amount of molecularly dissolved oxide depends on the age of the sol, rising to a maximum in a freshly formed sol and then gradually sinking.[14] The initial rise is due to the slow rate of solution, and the subsequent slow drop on aging is due to growth of the particles with a consequent decrease in solubility. The effect of aging accounts for the variations in solubility reported by different investigators. Moreover, the usual measurements made on the supernatant solution after agglomeration of sol are necessarily wrong since they fail to take into account the amount adsorbed by the hydrous particles during agglomeration.

<div align="center">PROPERTIES</div>

Color

Although vanadium pentoxide is said to exist in a yellow amorphous form and a red crystalline form, the observations reported in the preceding section indicate that degree of dispersion is the important factor in determining the color. The most highly dispersed oxide appears yellow, the color changing to reddish brown as the particles become larger and denser. If this view is correct, the reddish crystalline oxide should be yellow if sufficiently finely divided; and this proves to be the case. Wegelin[15] prepared a canary-yellow sol by prolonged trituration, in an agate mortar, of red-brown crystals of vanadium pentoxide obtained by allowing the molten oxide to cool slowly. If a sol prepared in this way is coagulated by the addition of a small amount of sodium chloride, the yellow precipitate shows little change of color on keeping; but if an excess of sodium chloride is used to effect coagulation, the resulting precipitate changes in color from yellow to reddish brown in the course of a few days. This transformation in color follows the growth and agglomeration of particles which take place more rapidly with increasing concentration of electrolyte in contact with the precipitate.

Double Refraction

Probably the most interesting property of vanadium pentoxide sol is the double refraction which it exhibits (1) on stirring, (2) on

[13] Gessner: Kolloid-Beihefte, 19, 213 (1924).

[14] Reinders and van der Lee: Rec. trav. chim., 47, 193 (1928); cf. Lange: Kolloid-Z. 59, 162 (1932).

[15] Kolloid-Z., 14, 65 (1914).

standing, (3) in a magnetic or electric field.   These will be considered
in order:

Streaming Double Refraction.   The phenomenon of double refrac-
tion on stirring, or streaming double refraction, has been given detailed
consideration by Freundlich and his pupils.   If stirred with a glass
rod and viewed in reflected light, an aged sol appears to be filled with
yellow, glittering streaks as if fine crystals were suspended in it.[16]   In
transmitted light the sol remains clear, but dark streaks can be
observed.   Viewed between crossed nicols, the field remains dark as
long as the sol is not disturbed, but stirring causes the field to become
bright at once.   By allowing the sol to flow between crossed nicols in
convergent light parallel to the line connecting the nicols, an image is
obtained of a crossed axis with concentric rings.   Observed with a
quarter-wave mica plate, the flowing sol behaves like a positive uni-
axial crystal.   Freundlich pictures the sol at rest as made up of elon-
gated particles possessing the usual unordered Brownian movement
which can give no double refraction.   The setting up of directed
motion causes the sol to lose its isotropic nature and to become double
refracting.   A section cut from the sol may be looked upon as having
a space lattice somewhat similar to a plate from an optically monoaxial
crystal, the long axis of the sol particles coinciding in direction with
the optical axis.

If the sol is rotated between two cylindrical walls and viewed
between crossed nicols, four minima of brightness are seen, giving the
appearance of a dark cross[17] the arms of which form an angle with
the direction of polarization.   The angle is independent of the con-
centration of sol but increases rapidly with increasing age of sol and
decreases with rise of temperature.   In a slowly moving fresh sol, the
angle has the value of 45°, and in a rapidly moving aged sol, it
approaches 90°.   This behavior of the so-called vortex cross has been
explained by Freundlich[18] in terms of the elasticity of the sol.[19]   In
fresh, slowly moving sols the elastic deformation of the sol elements
is small; hence the sol behaves like a rigid body and the cross-angle
is 45°.[20]   In an aged, rapidly moving sol the angle is close to 90°.   From
this point of view, the cross-angle is identical with the angle of maxi-

[16] Freundlich and Leonhardt: Kolloid-Beihefte, **7**, 207 (1915); Diesselhorst and
Freundlich: Physik. Z., **16**, 422 (1915); Freundlich: Z. Elektrochem., **22**, 27 (1916).
    [17] Zocher: Z. physik. Chem., **98**, 293 (1921).
    [18] Freundlich, Stapelfeldt, and Zocher: Z. physik. Chem., **114**, 161, 190 (1924);
cf., *however*, Mottsmith and Langmuir: Phys. Rev. (2) **20**, 95 (1922).
    [19] Freundlich and Seifriz: Z. physik. Chem., **104**, 233 (1923).
    [20] Schwedoff: J. phys. (3) **1**, 49 (1892).

mum deformation, and the direction of maximum deformation corresponds with the direction of the velocity gradient. Hence, the colloidal particles do not arrange themselves along the line of motion because of friction between adjacent liquid layers of different velocities, but place themselves in the direction of maximum deformation. Only in an aged sol moving with high velocity does the direction practically coincide with the direction of flow, giving a vortex cross with 90° angles.

The double refraction in an aged sol is so strong that it can be demonstrated by allowing the sol to flow through a prismatic trough with a triangular cross-section and using this as a prism to decompose spectrum lines. In this way, the red hydrogen line is resolved into two oppositely polarized lines. The more strongly refracted ray vibrates parallel to the direction of flow of the sol, and in accordance with Babinet's rule, this extraordinary ray is more strongly absorbed than the other.[21]

As already noted, the double refraction is not observed in a freshly prepared vanadium pentoxide sol. Freundlich[22] investigated quantitatively the influence of age of sol on its double refraction and found the velocity of aging, at constant streaming velocity and temperature, to be given by the equation $d\Delta/dt = K\Delta(\Delta_\infty - \Delta)^2$, where Δ is the double refraction. The magnitude of the velocity of aging is very sensitive to the action of impurities which may have either a stabilizing or peptizing action on the sol. With rising temperature the anisotropy decreases in a linear fashion. The double refraction of the sol corresponds approximately to the vanadium pentoxide content. The increase in double refraction with age is probably due to the disappearance of smaller V_2O_5 particles with consequent increase in the size of the larger ones. This aging is retarded by the presence of H_3AsO_4, which is adsorbed on the surface of the particles and interferes with the crystal growth.[23]

Examination of an aged sol with the cardioid ultramicroscope[24] reveals rod-like structures whose length is approximately thirty times the diameter. In a slit ultramicroscope, their axis deviates by less than 30° from a line perpendicular to the axis of the illuminating

[21] Cf., also, Humphry: Proc. Phys. Soc. (London) **35**, 217 (1923).

[22] Freundlich, Stapelfeldt, and Zocher: Z. physik. Chem., **114**, 161 (1924); cf. Gessner: Kolloid-Beihefte, **19**, 283 (1924).

[23] Freundlich and Dannenberg: Z. physik. Chem., **119**, 87 (1926).

[24] Kruyt: Koninklijke akad. Wetenschappen, Amsterdam, **18**, 1625 (1915); Kolloid-Z., **19**, 161 (1916).

beam. Reinders[25] believes that the appearance of birefringence on aging is due to the formation of ultramicroscopic needles, since he succeeded in demonstrating a similar birefringence in sols of mercurous chloride and lead iodide which ordinarily form microscopic crystals. Later, Zocher[26] established the crystalline character of the particles in an aged vanadium pentoxide sol by means of x-radiograms. The interference lines are broad, indicating the very small size of the crystals in the sol; but the arrangement of the lines is the same as observed with crystals obtained by cooling the molten pentoxide. The effect of aging on the dielectric constant of the sol[27] indicates that the growth of rod-shaped particles during the aging process is not an ordinary case of crystallization.[28] Freundlich[29] attributes the appearance of double refraction, on adding electrolytes to a benzopurpurine sol, to the development of longer particles by ordered coagulation and not to the growth of needle crystals. Just why we should get ordered coagulation into rod-shaped particles only in certain cases is not obvious.

The phenomenon of streaming double refraction is not confined to sols of vanadium pentoxide, but has been observed with an aged ferric oxide sol, soap solutions, clay suspensions, silver cyanate, and a number of dyes such as benzopurpurine, alizarin, and aniline blue.[30] In most of these, the double refraction appears to be due in large measure to the anisotropic nature of the particles themselves rather than to the lattice-like arrangement of rod-shaped isotropic particles. On the other hand, with tungsten trioxide sol, the form and size of the particles are the important factors in changing the nature of the Tyndall light, whereas the anisotropy of the particles is negligible.

Attention has been called to the greater adsorption of the extraordinary ray than of the ordinary ray by a streaming vanadium pentoxide sol. This gives rise to dichroism which may be termed streaming dichroism. When the intensity of transmitted polarized light, whose electric vector vibrates perpendicularly to the direction of flow of the sol, is decreased by allowing the sol to flow, the light appears redder. As a matter of fact, the spectrum of the flowing sol extends from 710 to 582 mμ; while at rest, it extends only to 558 mμ. With

[25] Koninklijke akad. Wetenschappen, Amsterdam, **19**, 189 (1916).

[26] Z. physik. Chem., **98**, 312 (1921).

[27] Errera: Kolloid-Z., **31**, 59 (1922); **32**, 373 (1923).

[28] Szegvari and Wigner: Kolloid-Z., **33**, 218 (1923).

[29] Freundlich, Schuster, and Zocher: Z. physik. Chem., **105**, 119 (1923).

[30] Zocher: Z. physik. Chem., **98**, 293 (1921); Freundlich, Schuster, and Zocher: **105**, 119 (1923).

parallel electric vector, the light appears yellower when the sol flows, the spectrum extending only to 542 mμ.[31]

Tactosols. From certain sols containing non-spherical particles a concentrated anisotropic phase settles toward the bottom of the vessel on standing, leaving a dilute isotropic phase above. This phenomenon has been observed with aged iron oxide[32] and benzopurpurine sols and especially with vanadium pentoxide sols.[33] The rod-shaped particles apparently arrange themselves parallel to each other in a kind of spindle-shaped globule. Sols which are capable of giving such anisotropic structures spontaneously are called tactosols, and the individual structures are called tactoids. The isotropic phase is called an atactosol. A satisfactory theory for the spontaneous formation of such anisotropic structures has not been formulated.

Magnetic and Electric Double Refraction. The double refraction resulting from the orientation of colloidal particles in a magnetic field has been considered in the case of ferric oxide sol which exhibits the phenomenon to a marked degree (p. 65). This property which is known as the Majorana phenomenon was observed in vanadium pentoxide sol by Freundlich[16] and has been studied in detail by Zocher[34] and Björnstahl.[35] The sol exhibits positive magnetic double refraction and dichroism both when freshly prepared and when aged, and both in tactosols and atactosols. The double refraction increases as the fourth power of the field strength and possesses no detectable temperature coefficient. Any variations from this simple rule are probably due in part to streaming orientation of the particles and in part to the elastic properties of the sol.

In an electric field, vanadium pentoxide sol exhibits double refraction,[36] positive with respect to the long axis of the particles which orient themselves parallel to the lines of force.

Errera[37] made the interesting observation that the dielectric constant increases with the double refraction. A 1.4% sol, one year old, had a dielectric constant of 400 as compared to 83 for water. The dielectric constant of a freshly prepared 0.012% sol increased in 20 days from 74.7 to 112.4. In these experiments the rod-shaped parti-

[31] Diesselhorst and Freundlich: Physik. Z., **16**, 419 (1915).

[32] Cotton and Mouton: Ann. chim. phys. (8) **11**, 145 (1907).

[33] Zocher: Z. anorg. Chem., **147**, 91 (1925); Zocher and Jacobsohn: Kolloid-Z., **41**, 220 (1927); Kolloid-Beihefte, **28**, 167 (1929).

[34] Z. physik. Chem., **98**, 311 (1921); Heller and Zocher: **A164**, 55 (1933).

[35] Thesis, Upsala (1924).

[36] Marshall: Trans. Faraday Soc., **26**, 173 (1930).

[37] Kolloid-Z., **31**, 59 (1922); **32**, 157 (1923).

cles were oriented parallel to the direction of the current; but it is not obvious how this changed the capacity in the direction of raising the dielectric constant.

Coagulation

Vanadium pentoxide is quite sensitive to the action of most electrolytes as evidenced by the relatively low concentration necessary to cause clouding of the sol within 5 minutes, the so-called "clouding value," Table XXI.[38] With but few exceptions the clouding value

TABLE XXI

CLOUDING VALUES OF VANADIUM PENTOXIDE SOLS

Electrolyte	Clouding value, milliequivalents per liter	Electrolyte	Clouding value, milliequivalents per liter
LiCl...............	130.0	$Sr(NO_3)_2$..........	0.56
NaCl..............	50.0	$BaCl_2$.............	0.46
NH_4Cl.............	25.0	$ZnSO_4$.............	1.68
KCl...............	17.0	$VOSO_4$............	1.26
RbCl..............	7.7	$Pb(C_2H_3O_2)_2$.......	0.62
$AgNO_3$.............	3.7	$CuSO_4$.............	0.78
Tl_2SO_4.............	0.51	$HgCl_2$.............	> 26.0
Guanadine nitrate....	5.0	$Ce(NO_3)_3$..........	0.039
Strychnine nitrate....	0.17	$Al_2(SO_4)_3$..........	0.00168
$Mg(NO_3)_2$..........	1.12	$Th(NO_3)_4$..........	0.0168
$CaCl_2$..............	0.50		

is lower the greater the valence of the precipitating cation, but ions of the same valence show the usual large variations from a constant value. The precipitated gel is very readily repeptized by washing, provided the precipitating ions are not too strongly adsorbed.

Wiegner and Marshall[39] observed quantitatively the coagulation of vanadium pentoxide sol by counting the rod-shaped particles which were oriented in the ultramicroscope by means of an alternating current, so that all the particles were visible. The rapid coagulation at the critical point is considerably more rapid than would be predicted from Smoluchowski's theory for spherical particles. This abnormal rate of coagulation of rod-shaped particles depends neither on the

[38] Freundlich and Leonhardt: Kolloid-Beihefte, **7**, 195 (1915).
[39] Z. physik. Chem., **A140**, 1, 39 (1929).

nature of the coagulating electrolyte nor the nature of the sol, since benzopurpurine sol with rod-shaped particles behaves in this respect like vanadium pentoxide sol. At the beginning, the rate of coagulation is greater the larger the initial number of particles in the sol and the higher the ratio of length to thickness of the particles. The slow coagulation of the sol with sodium chloride as the precipitating electrolyte is likewise proportionately more rapid in the earlier stages of the process and does not conform to Smoluchowski's theory (Vol. I, p. 89). This is not surprising in view of the fact that the sphere of action for rod-shaped particles is more difficult to define than for spherical particles with which the Smoluchowski theory is concerned. The viscosity of sols with rod-shaped particles likewise does not conform to Poiseuille's law.[40]

Vanadium pentoxide sols coagulate on thawing after freezing at temperatures of -5, -15, and $-21°$, but are completely stable if frozen at $-182°$ and then melted.[41] Apparently the coagulation takes place during the freezing process, and the very rapid rate of freezing at the temperature of liquid air does not allow sufficient time for agglomeration of the particles.

VANADIUM PENTOXIDE JELLIES

Freundlich and Leonhardt[38] first pointed out that a stiff jelly is obtained by electrolyte coagulation of a sol containing 5.8 g V_2O_5 per l. A jelly results also when the sol prepared by Biltz's method is rendered too pure by dialysis.[42] This might be expected in view of the strong tendency of the oxide in mass to adsorb water and swell. A fresh sol contains smaller and more hydrous primary particles and gives a more gelatinous precipitate than an aged sol. It is probable that the relatively rapid coagulation in the presence of electrolytes gives fibrils just as the slow agglomeration during a long interval gives the rod-shaped birefringent particles. Thus, vanadium pentoxide appears to possess in high degree the characteristics necessary for jelly formation. In accord with this, Rabinerson[43] obtained jellies containing as little as 0.009 and 0.0045% V_2O_5 by adding sodium chloride to the sol.

[40] Kruyt: Kolloid-Z. (Zsigmondy Festschrift) **36**, 218 (1925); cf., also, Gessner: Kolloid-Beihefte, **19**, 213 (1924).

[41] Diyachkovskii: Kolloid-Z., **59**, 76 (1932).

[42] Ghosh, Chakravarti, and Dhar: Z. anorg. Chem., **152**, 399 (1926); see, also, Prakash and Dhar: J. Indian Chem. Soc., **7**, 417 (1930); Prakash: **9**, 193 (1932).

[43] Kolloid-Z., **68**, 305; **69**, 66 (1934).

A thixotropic jelly results by coagulation of the sol with a suitable amount of sodium chloride solution.[44]   The dielectric constant of a thixotropic sol was about 7% greater than that of water and diminished by about 6% when it set to a jelly.[45]   From the smallness of the decrease, it seems altogether unlikely that the water molecules lose their freedom of motion to any appreciable extent when the sol-gel transformation occurs.   The decrease is probably due chiefly to the loss of power of free rotation by the rod-shaped particles of the pentoxide.

Warming slows down the setting time of a thixotropic sol and liquefies a firm thixotropic jelly by breaking up the gel structure. Dilute jellies first liquefy and then coagulate on warming.[43]

Roy[46] obtained Liesegang rings of mercuric iodide in vanadium pentoxide jelly.

LOWER OXIDES OF VANADIUM

Hydrous Vanadium Dioxide.   When a solution of vanadyl sulfate or chloride is treated cautiously with a cold solution of sodium carbonate, hydrous vanadium dioxide[47] comes down as a grayish white precipitate soluble in excess of precipitant.   The oxide takes up oxygen from the air and must be washed in an inert atmosphere. Dried over sulfuric acid, it is a black, amorphous mass exhibiting a glassy fracture when broken.   It happens to analyze approximately for $V_2O_4 \cdot 7H_2O$ when dried over sulfuric acid at room temperature and for $V_2O_4 \cdot 3H_2O$ when heated at 100°, but these formulas are, of course, purely accidental.   Gain[48] claims to have prepared a pale red, crystalline hydrate, $V_2O_4 \cdot 2H_2O$, by boiling a solution of the dioxide in sulfuric acid.   When kept out of contact with the moisture of the air, it loses its red color, becoming olive green.   The red and green preparations are said to be isomeric.   The dioxide is insoluble in water but dissolves in both acid and alkalis, forming vanadyl salts[49] and vanadites or hypovanadates,[50] respectively.

Hydrous Vanadium Sesquioxide.   Hydrous vanadium sesquioxide comes down as a dirty-green flocculent precipitate when an aqueous

[44] Jochims: Kolloid-Z., **41**, 218 (1927).
[45] Kallmann and Kreidl: Z. physik. Chem., **A159**, 322 (1932).
[46] Kolloid-Z., **54**, 190 (1931).
[47] Crow: J. Chem. Soc., **30**, 454 (1876).
[48] Compt. rend., **143**, 823, 1154 (1906); **146**, 403 (1908).
[49] Guyard: Bull. soc. chim. (2) **25**, 350 (1876).
[50] Koppel and Goldmann: Z. anorg. Chem., **36**, 281 (1903).

solution of vanadium trichloride is treated with ammonia.[51]   It is extremely instable in the air, oxidizing to the dioxide very quickly. The hydrous oxide precipitated and washed in an inert atmosphere has been used as the starting point in the preparation of a number of salts of trivalent vanadium.   It functions as a basic oxide only.

The other oxides of vanadium, V_2O, VO, and V_2O_3, do not occur in the hydrous form.

HYDROUS COLUMBIUM PENTOXIDE

The action of an acid on a solution of alkali columbate yields a white gelatinous mass of hydrous columbium pentoxide; it is also formed by hydrolysis of $CbCl_5$ or $CbOCl_3$.   When dried at room temperature it is a horny amorphous mass, and at $100°$ it is a white powder.   On heating rapidly to around $500°$ it exhibits the glow phenomenon, and definitely crystalline Cb_2O_5 is formed.[52]

The dehydration isobars for the gel obtained by acidifying alkali columbate were found by Hüttig and König[53] to be smooth curves showing no indication of a definite hydrate.   On the other hand, the curve for a preparation made by heating the precipitated oxide with water at $150°$ in a bomb tube showed a point of inflection which suggests the existence of either a monohydrate or a hemihydrate. Since none of the hydrous preparations give an x-ray diffraction pattern, the formation of a hydrate has not been established with certainty. If a hydrate is really formed by heating the hydrous oxide under pressure, prolonged treatment should yield a crystalline product.

Like hydrous vanadium pentoxide, the corresponding columbium oxide cannot be washed free from the mother liquor without undergoing peptization.   It dissolves but slightly in hydrochloric acid, but the residue obtained after boiling with excess acid is easily peptized by water, giving a sol from which practically all the hydrochloric acid can be removed by dialysis.   The sol gradually clouds on standing and is coagulated completely by electrolytes.[54]   The oxide thrown down from the hydrochloric acid sol with ammonia is an aged oxide corre-

[51] Locke and Edwards: Am. Chem. J., **20**, 594 (1898); Piccini and Brizzi: Z. anorg. Chem., **19**, 394 (1899).

[52] Böhm: Z. anorg. Chem., **149**, 217 (1925).

[53] Z. anorg. Chem., **193**, 93 (1930); cf., *however*, Süe: Compt. rend., **194**, 1745 (1932); Jander: Z. angew. Chem., **41**, 202 (1928).

[54] Wöhler: Pogg. Ann., **48**, 93 (1839); Marignac: Ann. chim. phys. (4) **13**, 20 (1868).

sponding to the so-called metatitanic acid. It is said to be a definite hydrate, $3Cb_2O_5 \cdot 4H_2O$,[55] but this is improbable.

Hauser and Lewite[56] prepared negative sols of both columbium and tantalum pentoxide by fusing the respective oxides with alkali in a silver crucible, dissolving the melt in water, and dialyzing for 10 to 12 days. Both sols are quite stable, even when heated, but are precipitated by all strong electrolytes except bases which stabilize them owing to preferential adsorption of hydroxyl ion. The two sols differ in their behavior toward carbon dioxide. If the gas is conducted into the tantalum pentoxide sol, complete coagulation takes place in a short time, whereas a sol of columbium pentoxide does not coagulate for a day under the same conditions. The Weiss-Landecker[57] method of separating columbium from tantalum is based on this difference in behavior of the sols. The method is of value only for the qualitative separation and detection of the elements.

HYDROUS TANTALUM PENTOXIDE

Gelatinous tantalum pentoxide is obtained by the hydrolysis of tantalum pentachloride with an excess of water and by treating sodium tantalate with acid. The gel exhibits the glow phenomenon when ignited, unless it has been aged by washing with hot water. A granular hydrous oxide is formed by fusing the anhydrous pentoxide with potassium bisulfate and boiling the resulting mass with water. The compounds prepared in different ways show a variable water content when dried at 100°. Formulas corresponding to hydrates have been suggested[58] for the dried oxide, but recent observations of Jander and Schulz[59] fail to establish their identity. The hydrous oxides investigated by Jander and Schulz were prepared by adding an excess of dilute nitric acid drop by drop to a solution of sodium tantalate of the composition $7Na_2O \cdot 5Ta_2O_5 \cdot 40H_2O$, at 0 and at 100°. The voluminous, amorphous precipitates were filtered on a membrane filter,[60] washed with large amounts of water, and dried in vacuum over sulfuric acid. The vapor-tension isotherms

[55] Santesson: Bull. soc. chim. (2) 24, 52 (1875).

[56] Z. angew. Chem., 25, 100 (1912).

[57] Z. anorg. Chem., 64, 65 (1909).

[58] Rose: Pogg. Ann., 100, 417 (1857); 106, 141 (1859); Rammelsberg: 136, 177, 352 (1869); Hermann: J. prakt. Chem., 70, 195 (1857); (2) 5, 66 (1872).

[59] Z. anorg. Chem., 144, 225 (1925).

[60] Zsigmondy and Bachmann: Z. anorg. Chem., 103, 119 (1918); Zsigmondy and Jander: Z. anal. Chem., 58, 241 (1919); Jander and Jander: 63, 273 (1923).

were determined in the vacuum apparatus described by Zsigmondy.[61] The results recorded in Fig. 50 show a continuous variation in the water content of the oxide with changing vapor pressure of the surroundings, thereby rendering the existence of hydrates improbable.
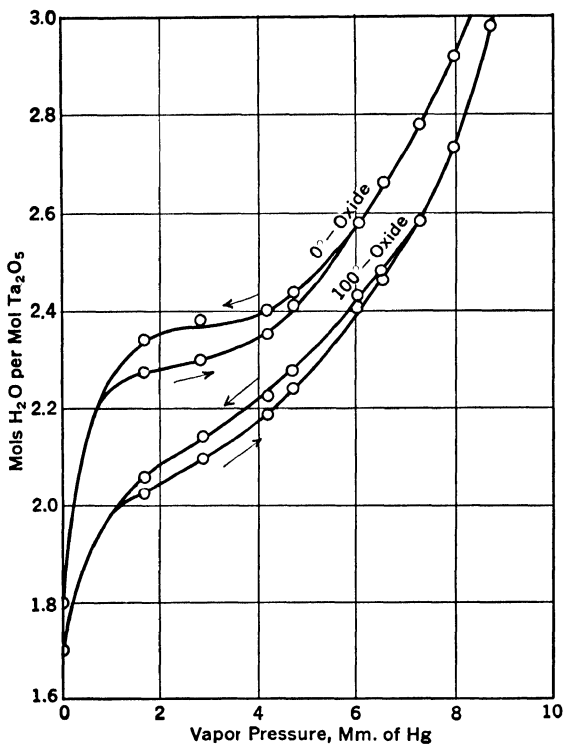
FIG. 50.—Vapor pressure isotherms for hydrous tantalum pentoxides.

The rehydration and redrying curves are similar qualitatively to those observed by van Bemmelen and Anderson with the gels of stannic oxide, silica, etc. (p. 196). The hysteresis cycle of the 100°-oxide is smaller than that of the 0°-oxide and is displaced more toward the side of lower water content. The optical phenomena so characteristic of the hydration and dehydration of silica were lacking in the tantulum pentoxide gels; both remained white and chalky under all conditions.

Jander and Schulz[62] observed that, under a given set of conditions, the gel always had more than $1.4H_2O$ to $1Ta_2O_5$. This caused them to weaken to the point of suggesting that the gel was essentially a hydrous pentatantalic acid of the formula $H_7Ta_5O_{16}$. Hüttig and König[63] fell in line with this suggestion in spite of the fact that in every case the dehydration isobars followed a smooth course until well below the composition $Ta_2O_5 \cdot H_2O$. In certain isobars, however,

[61] Zsigmondy, Bachmann, and Stevenson: Z. anorg. Chem., **75**, 189 (1912).

[62] Kolloid-Z. (Zsigmondy Festschrift) **36**, 109 (1928); Jander: Z. angew. Chem., **41**, 202 (1928).

[63] Z. anorg. Chem., **193**, 100 (1930).

a point of inflection was observed which suggested the formation of either a monohydrate or a hemihydrate. As in the case of columbium pentoxide, the evidence is not conclusive, and the work should be continued.

Sols of hydrous tantalum pentoxide are obtained in the same way as the corresponding columbium pentoxide sols just described. The hydrous oxide is insoluble in water but is slightly acidic in character, dissolving in alkali with the formation of tantalate.

HYDROUS ANTIMONY PENTOXIDE

On account of the position of antimony in the periodic system of the elements, antimony pentoxide is usually supposed to form ortho-, pyro-, and metaantimonic acids: H_3SbO_4 or $Sb_2O_5 \cdot 3H_2O$, $H_4Sb_2O_7$ or $Sb_2O_5 \cdot 2H_2O$, and $HSbO_3$ or $Sb_2O_5 \cdot H_2O$,[64] corresponding to the acids of phosphorus. In addition to these, hydrates containing 4, 4.5, 5, and 6 mols of water per mol of pentoxide have been described.[65] The oxide is thrown down in a flocculent, hydrous condition by hydrolyzing antimony pentachloride in water or antimony trichloride in nitric acid solution; and by decomposition of a solution of potassium pyroantimonate with acids. A survey of the procedures that must be followed to get a composition approximating a hydrate suggests that the so-called ortho-, pyro-, and metaantimonic acids are, in reality, hydrous antimony pentoxides dried under such conditions that the composition approaches that of the corresponding acids of phosphorus. This conclusion was confirmed by Simon and Jander,[66] who obtained vapor pressure-composition diagrams for hydrous antimony pentoxides similar to those for hydrous tantalum pentoxides shown in Fig. 50. Oxides prepared at 0, 60, and 100° all showed the characteristic hysteresis region in the vapor pressure curves. The 100°-oxide exhibited optical phenomena in this region similar to those observed by van Bemmelen with hydrous silica. At the beginning of rehydration the oxide was a transparent glassy mass; as more water was taken up, it became cloudy and the color changed to brown; on complete hydration, the gel was clear and colorless once more.

[64] *See* Fremy: J. prakt. Chem., **45**, 209 (1848); Hefftner: Pogg. Ann., **86**, 419 (1852); Geuther: J. prakt. Chem. (2) **4**, 438 (1871); Daubrawa: Ann., **186**, 110 (1877); Conrad: Chem. News, **40**, 157 (1879); Senderens: Bull. soc. chim. (3) **21**, 47; Delacroix: 1049 (1899).

[65] Senderens: Bull. soc. chim. (3) **21**, 47 (1899).

[66] Kolloid-Z., **23**, 122 (1918); Z. anorg. Chem., **127**, 68 (1923).

Although the isothermal dehydration curves indicate that no hydrate of antimony pentoxide exists, dehydration isobars obtained more recently by Simon and Thaler[67] furnish fairly conclusive evidence of the formation of a hydrate $3Sb_2O_5 \cdot 5H_2O$. Two of the curves are reproduced in Fig. 51. The 0°-curve is for an oxide thrown down when $SbCl_3$ is added slowly to chlorine water at 0°. A similar curve was obtained for a preparation several years old. The 300°-
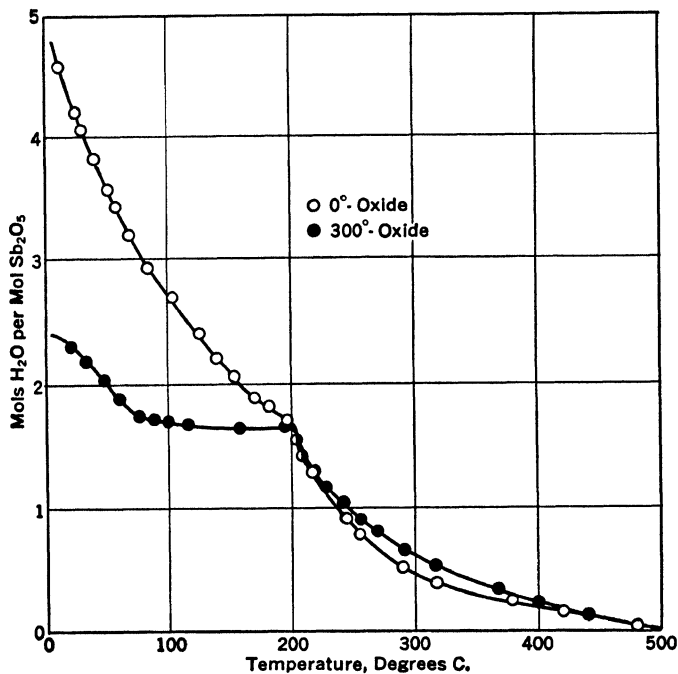
FIG. 51.—Dehydration isobars for two samples of hydrous $3Sb_2O_5 \cdot 5H_2O$.

curve is for the oxide prepared by heating the 0°-oxide with water at 300° in a bomb tube. The slight change in direction of the curve for the 0°-oxide at the composition $3Sb_2O_3 \cdot 5H_2O$ becomes a definite break in the curve for the 300°-oxide.

Like hydrous stannic oxides, the different antimony pentoxides adsorb alkali salts and phosphoric acid, giving typical adsorption isotherms. As would be expected, the loose, finely divided 0°-oxide has the highest adsorption capacity, and the dense, granular 100°-

[67] Z. anorg. Chem., 161, 113 (1927).

oxide has the lowest adsorption capacity for salts as well as water. The hydrous oxides adsorb alkalis from dilute solutions, giving amorphous masses of indefinite composition that have been mistaken for definite antimonates. More concentrated solutions dissolve the oxides, and from these solutions, definite crystalline antimonates are obtained.

Alcogels of antimony pentoxide are formed by treating the hydrogels with gradually increasing amounts of alcohol. If maintained over glycerol, dealcoholation curves are obtained similar to those of dehydration.

Hydrous oxides freshly prepared by hydrolysis of antimony pentachloride are peptized by thorough washing, forming instable sols from which an aged oxide gradually separates on standing or heating. Delacroix[68] and Senderens[65] mistook these sols for molecular solutions, and so reported erroneous values for the solubility of antimony pentoxide in water.

HYDROUS ANTIMONY TRIOXIDE

Like phosphorus trioxide, antimony trioxide is supposed to form ortho-, pyro-, and metaantimonous acids, H_3SbO_3 or $Sb_2O_3 \cdot 3H_2O$, $H_4Sb_2O_5$ or $Sb_2O_3 \cdot 2H_2O$, and $HSbO_2$ or $Sb_2O_3 \cdot H_2O$, respectively. Clarke and Stallo[69] claim to have prepared the trihydrate or orthoacid by the action of sulfuric acid on barium antimony tartrate. The addition of mineral acids to tartar emetic yields a hydrous product containing varying amounts of adsorbed tartaric acid and precipitating agent which are difficult to remove by washing.[70] Using alkali carbonates, acetates, phosphates, and tungstates as precipitants, Long[71] found the composition to be approximately $Sb_2O_3 \cdot 0.5H_2O$. Schaffner[72] reported the formation of a dihydrate, pyroantimonous acid, by treating an alkali solution of arsenious sulfide with copper sulfate, until all the sulfur is removed, and then acidifying. Lea and Wood[73] found that the method of Clarke and Stallo does not yield orthoantimonous acid but a hydrous oxide of varying composition, depending on how it is washed and dried. Long's method likewise yielded products of varying water content, depending on the

[68] Bull. soc. chim. (3) 21, 1049 (1899); 25, 288 (1901).
[69] Ber., 13, 1792 (1880).
[70] Guntz: Compt. rend., 102, 1472 (1886).
[71] J. Am. Chem. Soc., 17, 87 (1895).
[72] Ann., 51, 168 (1844); cf., however, Serono: Gazz. chim. ital., 24, 274 (1894).
[73] J. Chem. Soc., 123, 259 (1923).

temperature of precipitation. Dehydration isobars for the oxides thrown down at 0, 60, and 100°, from tartar emetic solution with hydrochloric acid, were smooth curves indicating the absence of definite hydrates.[74]

The oxide precipitated with mineral acids contains more adsorbed impurities and retains its adsorbed water more strongly than the compound precipitated with alkalis and alkali carbonates. By treating a solution of antimony trichloride in hydrochloric acid with ammonia, a very finely divided hydrous mass is first formed which goes over to anhydrous oxide on warming.

Antimony trioxide is insoluble in water but is amphoteric in character, giving antimonous salts with acids and antimonate with alkalis. Heated in air, the trioxide takes on more oxygen, giving the tetraoxide, Sb_2O_4. No oxides between Sb_2O_4 and Sb_2O_5 exist.[75]

HYDROUS BISMUTH TRIOXIDE HYDRATE

Bismuth is precipitated quantitatively in the cold as a white flocculent mass which is either hydrous $Bi_2O_3 \cdot 3H_2O$ [$Bi(OH)_3$] or hydrous $Bi_2O_3 \cdot 2H_2O$. If thrown down from chloride or nitrate solution, the hydrous hydrate is usually contaminated by oxychloride or oxynitrate; but if the solution of the oxide in alkali in the presence of glycerol[76] is acidified, the compound comes down in a highly gelatinous form free from basic salt.[77] A better procedure consists in dropping the glycerol solution slowly into cold water.[78] Fairly pure preparations are said to result also by pouring a solution of bismuth nitrate into dilute alkali,[79] and by precipitating an acid solution of bismuth nitrate with concentrated ammonia.[80]

Dehydration isobars for two electrolyte-free precipitates (method of Corfield and Woodward[78]) were obtained by Hüttig, Tsuji, and Steiner.[81] The curves are reproduced in Fig. 52. The precipitate gives a distinctive diffraction pattern entirely different from the pattern of the anhydrous oxide. It is therefore a definite hydrate; but from these observations it is not obvious whether it is a trihydrate or a dihydrate. Hüttig believes it to be $Bi_2O_3 \cdot 3H_2O$ or $Bi(OH)_3$,

[74] Simon and Poehlmann: Z. anorg. Chem., **149**, 101 (1925).

[75] Simon and Thaler: Z. anorg. Chem., **162**, 253 (1927).

[76] Löwe: Z. anal. Chem., **22**, 498 (1883).

[77] Thibault: J. Pharm. (6) **12**, 559 (1900).

[78] Corfield and Woodward: Pharm. J. (4) **113**, 84 (1924).

[79] Prideaux and Hewis: J. Soc. Chem. Ind., **41**, 167T (1922).

[80] Moles and Portillo: Chem. Zentr., I, 33 (1924).

[81] Z. anorg. Chem., **200**, 74 (1931).

but the dehydration isobars point more strongly to its being a dihydrate. To settle this question, relatively large crystals of the compound should be prepared and subjected to isobaric dehydration.

A positive sol of the bismuth hydrate results on dialyzing a dilute solution of bismuth nitrate containing nitric acid.[82] The sol is but slightly opalescent, is almost neutral, and gives only the faintest test for nitrate. A very stable sol is formed by adding alkali to a solution of bismuth nitrate in glycerol containing Paal's sodium salts of lysalbinic and protalbinic acids. After purification by dialysis, this sol can be evaporated in vacuum at 60°, giving a gel that can be repeptized in water. The hydrous gel precipitated from antimony
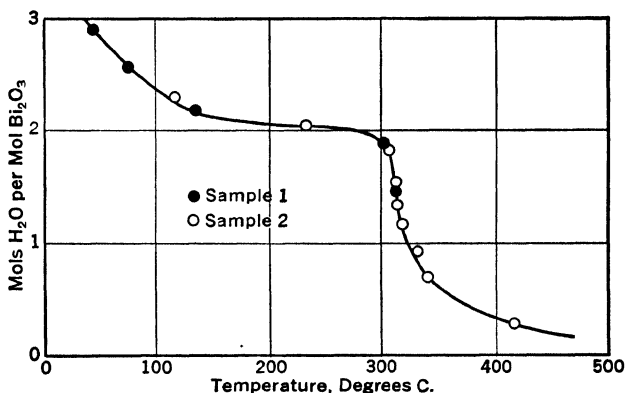
FIG. 52.—Dehydration isobar for $Bi_2O_3 \cdot 2H_2O$.

nitrate solution with concentrated alkali can be peptized by thorough washing.[83] The resulting sol is more stable in the presence of sucrose, mannitol, glycerol, and lactose.[84] The last two substances appear to react chemically with the hydrous oxide.

HIGHER OXIDES OF BISMUTH

If a current of chlorine is passed into an alkali in which hydrous bismuth trioxide is suspended, a reddish powder results which is supposed to be anhydrous or hydrous Bi_2O_4. Similarly, highly oxidized products are formed by the electrolytic oxidation of the trioxide and

[82] Biltz: Ber., **35**, 4434 (1902).

[83] Kühn and Pirsch: Kolloid-Z. (Zsigmondy Festschrift) **36**, 310 (1925).

[84] Cf. Sen and Dhar: Kolloid-Z., **33**, 193 (1923); cf., also, Ostwald and Rödigu: **49**, 412 (1929).

by the action of persulfates, hydrogen peroxide, and potassium ferricyanide on the trioxide in the presence of alkali.[85]   According to Gutbier and Bünz,[86] none of these reactions gives a definite homogeneous product.

Worsely and Robertson[87] claim to have obtained the tetroxide pure, by oxidizing the trioxide suspended in dilute alkali and freeing the resulting product from trioxide and alkali by triturating with glacial acetic acid.   Two isomeric monohydrates are described, one brown and the other purplish black.   Using concentrated alkali and chlorine, a mixture of yellow tetroxide dihydrate and red or brown pentoxide monohydrate is said to form.   Ammonium persulfate is said to give some hexoxide.   The observations are incomplete, if not inaccurate, in many respects.   It seems altogether unlikely that the alleged hydrates are anything but indefinite hydrous oxides.

[85] Muir and Carnegie: J. Chem. Soc., **51**, 77 (1887); Deichler: Z. anorg. Chem., **20**, 81 (1899); Hauser and Vanino: **39**, 381 (1904); Moser: **50**, 33 (1906); Ruff: **57**, 220 (1908).

[86] Z. anorg. Chem., **48**, 162, 294; **49**, 432 (1906); **50**, 210; **52**, 124 (1907); Gutbier and Micheler: **59**, 143 (1908).

[87] J. Chem. Soc., **117**, 63 (1920).

CHAPTER XII

THE HYDROUS OXIDES AND HYDRATES OF MOLYBDENUM, TUNGSTEN, AND URANIUM

HYDROUS MOLYBDENUM TRIOXIDE

Molybdenum trioxide forms two and only two [1] crystalline hydrates: $MoO_3 \cdot 2H_2O$ or H_4MoO_5, and $MoO_3 \cdot H_2O$ or H_2MoO_4. The dihydrate separates at room temperature in yellow crusts from a nitric acid solution of ammonium molybdate such as is used in the estimation of phosphorus. By heating to 40 to 50° a solution of dihydrate or the solid suspended in water, Rosenheim and Davidsohn [2] obtained what they called α-$MoO_3 \cdot H_2O$ to distinguish it from β-$MoO_3 \cdot H_2O$ which comes down at 65 to 70°. Both preparations crystallize in fine white needles, but the so-called α-oxide differs from the β-oxide in forming with water a stable milky suspension or sol and in losing all its hydrate water at a lower temperature. It is probable that the differences between the two preparations are due to variations in the size and physical character of the primary particles thrown down at different temperatures, rather than to allotropy. Doubtless this could be settled by an x-ray study of the crystal structure of the two preparations such as Burger [3] used to establish the chemical individuality of $MoO_3 \cdot H_2O$ and MoO_3.

MOLYBDENUM TRIOXIDE SOL

Graham [4] first recognized the existence of a sol of the trioxide which he prepared by dialysis of a 5% solution of sodium molybdate acidified with a slight excess of hydrochloric acid. During dialysis, this sol behaves like hydrous ceric oxide in setting to a jelly which subsequently liquefies as the dialysis is continued. The sol is very stable toward electrolytes, has a yellow color and an astringent taste, and is acid to

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[1] Hüttig and Kurre: Z. anorg. Chem., **126**, 167 (1923).
[2] Z. anorg. Chem., **37**, 314 (1903).
[3] Z. anorg. Chem., **121**, 240 (1922).
[4] Ann., **135**, 65 (1865).

litmus. By evaporating in vacuum over sulfuric acid, a glassy hydrous mass is obtained which is readily taken up again by water.[5] Graham's observations were confirmed by Sabanejew,[6] Linebarger,[7] and Lottermoser;[8] but Bruni and Pappadà[9] failed to get a sol by dialysis of a nitric acid solution of ammonium molybdate having the composition of the phosphoric acid reagent. Rosenheim and Bertheim[10] likewise claimed that the solutions formed by shaking $MoO_3 \cdot 2H_2O$ with water are not colloidal since at every temperature the oxide possesses a definite solubility. However, such solutions saturated at high temperature do not crystallize out on cooling even when stirred for a long time with crystals of dihydrate. Indeed, a solution saturated at 100° is fortyfold supersaturated on cooling to room temperature. Cryoscopic determinations on such a solution indicate a molecular weight for the trioxide in solution of approximately 600, which is of the same order as Sabanejew obtained for the Graham sol. This fact, together with the observed high conductivity and high hydrogen ion concentration of the dihydrate solution, led to the conclusion that solutions of $MoO_3 \cdot 2H_2O$, whether prepared directly or by the method of Graham, are not colloidal. This conclusion was called in question by Wöhler and Engels,[11] who demonstrated the heterogeneity not only of Graham's sol but also of the nitric acid solution of ammonium molybdate and of the aqueous solutions of $MoO_3 \cdot 2H_2O$ saturated in the hot or in the cold. All these solutions contained particles clearly visible in the ultramicroscope, which were precipitated by the addition of gelatin but not by electrolytes. In the light of their observations, Wöhler and Engels classify the solutions as semicolloidal, since they appear to lie in the borderland between true crystalloidal solutions and hydrophile sols. This disposition of the matter fails to emphasize the important fact that $MoO_3 \cdot 2H_2O$ is soluble to a certain extent and hence, under different conditions, it may be chiefly in solution or chiefly colloidal.[12] A newly formed solution of sodium molybdate acidified with hydrochloric acid will contain more oxide in solution than an old preparation, since aging brings about an increase in size and a decrease in solubility

[5] Cf. Ullik: Sitzber. Akad. Wiss. Wien, **60**, 302 (1870).

[6] Ber., **23**, 87 (1890).

[7] Am. J. Sci. (3) **43**, 222 (1892).

[8] "Uber anorg. Kolloide," Stuttgart, 11 (1901).

[9] Gazz. chim. ital., **31** I, 244 (1901).

[10] Z. anorg. Chem., **34**, 427; Rosenheim and Davidsohn: **37**, 314 (1903)

[11] Kolloid-Beihefte, **1**, 466 (1910).

[12] Cf. Rabinovich and Kargin: Z. physik. Chem., **A152**, 24 (1931).

of the colloidal particles. In all preparations, the particles are relatively small and their solution pressure is sufficiently large to make the mixture distinctly acid and a good conductor. But a part of the hydrate is suspended in the liquid and does not contribute to the acidity of the solution. The lowering of the vapor pressure of such mixtures is due in large measure to the dissolved oxide and not to the suspended particles; hence, molecular weights deduced from cryoscopic measurements under the assumption that all the oxide is dissolved are necessarily erroneous.

Travers and Malaprade[13] determined the molecular weight of the molybdenum trioxide in solutions cryoscopically, and found it to be 593, confirming the earlier observations of Sabanejew and of Rosenheim. From these observations Travers and Malaprade conclude that the formula is $4MoO_3 \cdot H_2O$.[14] They admit, however, that the solution probably contains polymerized molecules $(4MoO_3 \cdot H_2O)_x$. The only reason for assigning the above formula for the oxide in solution is that the calculated molecular weight is 594 as compared with the observed value 593. The latter value means nothing if the solutions contained any appreciable amount of polymerized molecules or colloidal aggregates, and it probably contained both. Moreover, the part in molecular solution is highly ionized and this was not taken into account in deducing the formula from the alleged molecular weight. Jander[15] assumed that the first stage in the polymerization with increasing hydrogen ion concentration is trimolybdic acid, then hexamolybdic acid, followed by twelve and twenty-four aggregates.

Bhatia, Ghosh, and Dhar[16] mixed equivalent amounts of ammonium molybdate to make a solution which would contain 15.5 g $MoO_3 \cdot H_2O$ or H_2MoO_4. This was ultrafiltered at once, and 52% did not pass the filter. This means that at least 52% was colloidally dispersed, and probably more. The amount of colloidal acid increased with the time, and the specific conductivity decreased owing to polymerization.

Rosenheim heated to 50° a solution containing hydrochloric acid and sodium molybdate in the ratio of 4 : 1. From this solution a slimy hydrous mass precipitated which was readily peptized by water after thorough washing. The particles in this sol were larger than in the Graham sol, and unlike the latter it was slightly opalescent

[13] Bull. soc. chim. (4) 39, 1408 (1926); Compt. rend., 183, 292 (1926).

[14] Cf. Diyachkovskii and Dumanskii: J. Russ. Phys.-Chem. Soc., 58, 630 (1926).

[15] Metallbörse, 20, 1855 (1930); cf. Novoselova: J. Gen. Chem. (U.S.S.R.) 1, 668 (1931).

[16] Z. anorg. Chem., 184, 135 (1929).

and was precipitated in flocs by the addition of solutions of neutral salts and weak acids.

HYDROUS DIMOLYBDENUM PENTOXIDE

The hydrous oxide of pentavalent molybdenum is thrown down by adding ammonia to a hydrochloric acid solution of MoO_3 previously reduced with metallic molybdenum[17] or with hydriodic acid.[18]   At one time these were thought to be oxides of tetravalent molybdenum, but Klason[19] obtained a compound with identical properties by adding ammonia to a dilute solution of $(NH_4)_2MoOCl_5$ in which the molybdenum is pentavalent.   The precipitate is distinctly gelatinous; but it is said to have the composition $MoO(OH)_3$ when dried over phosphorus pentoxide.   When newly formed, it is very similar in physical character and color to hydrous ferric oxide, and like the latter it is peptized by thorough washing, forming a clear sol which varies in color from yellow to dark red depending on the concentration.   The sol gives a gelatinous precipitate with electrolytes, but it is probable that it could be precipitated as a jelly since Berzelius obtained a transparent jelly simply by allowing a dark red sol to stand for a month in a closed vessel.

Freundlich and Leonhardt[20] studied the properties of a sol prepared by peptizing the hydrous oxide thrown down with ammonia from a very dilute solution containing pentavalent molybdenum. The precipitate as well as the sol oxidizes to molybdenum blue more readily than Berzelius' preparation, probably on account of the difference in size of the particles.   The negatively charged sol agglomerates fractionally on adding electrolytes, and the last traces of sol are thrown down only by relatively high concentrations of multivalent cations that ordinarily precipitate in low concentrations.   This behavior is accounted for by the wide variation in the size of the colloidal particles; the larger particles agglomerate first, leaving a very dilute, highly dispersed sol which is not readily precipitated. In this respect, it is like Péan de St. Gilles' ferric oxide sol.[21]   It resembles it also in that the precipitation is readily reversible when the precipitating ions are weakly adsorbed, and almost irreversible when the precipitating ions are strongly adsorbed.

[17] Berzelius: Pogg. Ann., 6, 369, 389 (1826).
[18] Péchard: Compt. rend., 118, 804 (1894); Ann. chim. phys. (6) 28, 537 (1893).
[19] Ber., 34, 148 (1901).
[20] Kolloid-Beihefte, 7, 172 (1915).
[21] Weiser: J. Phys. Chem., 24, 312 (1920); 25, 672 (1921).

MOLYBDENUM BLUE

PRECIPITATED MOLYBDENUM BLUE

When a solution of MoO_3 or an acidified molybdate is reduced by hydrogen sulfide, sulfur dioxide, stannous chloride, metallic molybdenum, zinc, or other reducing agent, a deep-blue solution results, which deposits a blue, highly hydrous precipitate known as molybdenum blue. A similar product is obtained by the oxidation of lower oxides such as MoO_2, and by adding a cold dilute solution of MoO_2 in hydrochloric acid to a solution of ammonium molybdate. The last method of preparation suggests that the blue compound is a molybdenum molybdate such as $MoO_2 \cdot 2MoO_3$; but much doubt exists as to its composition. Marchetti[22] believes it to be $Mo_3O_8 \cdot 5H_2O$; Guichard,[23] $Mo_5O_{14} \cdot 6H_2O$; Junius,[24] Mo_7O_{20}; Zinzadzé,[25] $MoO_2 \cdot 4MoO_3 \cdot xH_2O$; whereas Bailhache[26] and Klason[27] believe that there are a number of blues which Klason regards as complex derivatives of Mo_2O_5 and MoO_3 analogous to phosphomolybdic acid. The evidence for the existence of different compounds is based largely on analytical differences that are probably of the same order of magnitude as the experimental errors inherent in analyzing a colloidal mass; hence, whether there is an individual blue or a number of related compounds, the composition is known only approximately. Marchetti[28] claims to have prepared a crystalline oxide having the formula $Mo_3O_8 \cdot 5H_2O$ by the cathodic reduction of a hydrochloric acid solution of MoO_3 and subsequent evaporation to crystallization. Munro[29] likewise reported the preparation of cubic crystals of molybdenum blue by dialyzing the sol, precipitating the gel with ammonium chloride, and evaporating the blue supernatant solution to dryness. The formula of the air-dried gel was approximately $Mo_3O_8 \cdot H_2O$, but since it is readily soluble in alcohol, Munro is convinced that it is not a hydrate but is Mo_3O_8 with adsorbed water.

[22] Z. anorg. Chem., **19**, 390 (1899); Muthmann: Ann., **238**, 108 (1887).

[23] Ann. chim. phys. (7) **23**, 498 (1901); Berzelius: Pogg. Ann., **6**, 385 (1826).

[24] Z. anorg. Chem., **46**, 428 (1905).

[25] Bull. soc. chim. (4) **49**, 872 (1931); Denigès: Compt. rend., **184**, 687; **185**, 777 (1927); Bull. soc. chim. (3) **3**, 797 (1890).

[26] Compt. rend., **133**, 1210 (1901).

[27] Ber., **34**, 153 (1901).

[28] Z. anorg. Chem., **19**, 391 (1899).

[29] Proc. Trans. Nova Scotian Inst. Sci., **16**, 9 (1928).

MOLYBDENUM BLUE SOL

Formation and Properties

Biltz[30] prepared a stable sol by reduction with hydrogen sulfide of an ammonium molybdate solution acidified with sulfuric acid, and subsequent dialysis. Dumanskii[31] made ultramicroscopic observations on a fairly pure sol prepared in this way and observed submicrons in rapid motion, if the sol was not too dilute; but on high dilution, it appeared optically empty. Dumanskii also prepared an electrolyte-free solution by reducing pure MoO_3, suspended in water, with metallic molybdenum. This appeared optically empty in the ultramicroscope, and from the freezing-point lowering, the molecular weight was calculated to be 440 ($Mo_3O_8 = 416$). From similar observations, Marchetti[22] calculated the molecular weight to be 460. The addition of small amounts of electrolytes caused submicrons to appear. Dumanskii concluded, therefore, that very pure molybdenum blue dissolves in water forming a true solution, but the presence of a small amount of electrolyte polymerizes the molecules. Since the blue as usually prepared contains adsorbed impurities, its solutions are colloidal. These observations of Dumanskii should be confirmed, for if the facts are as stated, they raise the question of the mechanism of the agglomeration of monomolecular molecules by the presence of small amounts of a variety of electrolytes.

The sol of molybdenum blue, prepared by Biltz's method, is negatively charged and so is precipitated by positively charged hydrous oxide sols of iron, aluminum, chromium, thorium, zirconium, and cerium. Particularly beautiful and stable color lakes with the hydrous oxides of aluminum, thorium, and cerium are formed by the mutual precipitation of the oppositely charged sols.

The blue coloration resulting from the reduction of a solution of hexavalent molybdenum is so sensitive that it is used in colorimetric analytical procedures. Thus the sensitivity of the tin test is 1 part in 1,423,000;[29] and under suitable conditions, 1 part of copper or antimony in 350,000 gives a blue coloration.[32] The color intensity on reduction of molybdic acid in the presence of phosphoric or arsenic acid is proportional to the phosphorus or arsenic content provided the concentration of the latter is between 0.001 and 0.1 mg per 100 cc.

[30] Ber., **37**, 1095 (1904).
[31] Kolloid-Z., **7**, 20 (1910).
[32] Feigl: Z. anal. Chem., **61**, 454 (1922).

This makes it possible to estimate small amounts of phosphoric and arsenic acids colorimetrically.[33]

Adsorption from Sol

Sols of molybdenum blue act as a dye bath, imparting a blue color to various fibers. Biltz[34] studied the influence of concentration of sol on the amount of blue oxide taken up by silk, cotton, and hydrous alumina. The results are given in Fig. 53. The uniform nature of the curves shows that the colored fibers and lake are "adsorption compounds," the composition of which varies continuously with the concentration of sol. The isotherms of adsorption are very similar to those obtained for organic colloidal dyestuffs such as benzidine[35] and benzopurpurine,[36] and for dyes in true solutions such as picric acid[37] and Congo red. In view of these observations, there is no longer any question but that dyeing by many organic and inorganic dyestuffs is essentially an adsorption process rather than a chemical process of the usual type, or a solid-solution phenomenon.
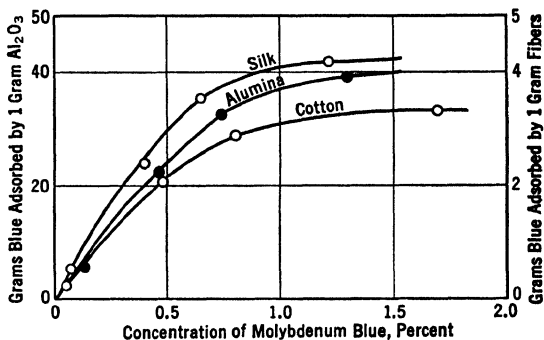
FIG. 53.—Adsorption of molybdenum blue by silk, cotton, and alumina.

With true solutions of dyes, one is not surprised to find a continuous increase in the amount of dye taken up with increasing concentration of the dye bath, in accord with the adsorption isotherm. But in colloidal solutions of dyes, the particles constitute a second phase in the ordinary sense of the term, and it is not obvious why they should fail to act like a phase of constant composition instead of the adsorption varying continuously with the apparent concentration of the bath.

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[33] Feigl: Z. anal. Chem., **61**, 454 (1922); Denigès: Compt. rend., **184**, 687; **185**, 777 (1927); Bull. soc. chim. (3) **3**, 797 (1890); for further applications of the reaction see Malowan: Z. anal. Chem., **84**, 209 (1931).

[34] Ber., **37**, 1766 (1904); **38**, 2963 (1905).

[35] Georgievics: Monatsh., **15**, 705 (1894); Georgievics and Löwy: **16**, 345 (1895).

[36] Freundlich and Losev: Z. physik. Chem., **59**, 284 (1907).

[37] Walker and Appleyard: J. Chem. Soc., **69**, 1334 (1896).

Bancroft[38] has gotten around this difficulty by accepting, with reservations, the physicists' view that, according to the kinetic molecular theory, a suspended particle should behave like a molecule in true solution (Vol. I, p. 63). If this is true, it will account for the marked similarity in the isotherms of adsorption for colloidal and molecular solutions.

Although recognizing the value, at some times, of treating a colloidal solution as having some of the properties of a true solution, Bancroft emphasizes the importance of distinguishing between the two at other times. In the same way, it is useful to treat a solid solute as behaving in certain respects like an ideal gas, but this does not mean either that the solute behaves in all respects like an ideal gas or that it is an ideal gas. In most cases the distinction between true and colloidal solutions can be made by applying the criterion of Gibbs. According to Gibbs, an apparent phase is not a one-phase system unless the properties are clearly defined when the temperature, pressure, and concentrations are fixed. By applying this test, it may be shown readily that most colloidal solutions are two-phase systems. The difficulty comes with solutions of such substances as tannin and soaps which appear to satisfy Gibbs' criterion for a one-phase system when in reality they are two-phase systems. A similar situation is encountered with a mixture of two gases which, in the last analysis, is neither physically nor chemically homogeneous but which is a one-phase system, nevertheless. To take care of these cases, Bancroft assumes that any gas or vapor will pass through any pore through which any other gas or vapor will pass. If this unproved but reasonable assumption is granted, it leads directly to the conclusion that any substance which can be filtered out by an ultrafilter is in colloidal solution and not in true solution, an ultrafilter being defined as a porous membrane which shows no marked negative adsorption, that is, specific adsorption of the solvent. This criterion puts soap and tannin in the list of colloidal solutions and would undoubtedly take care of the highly dispersed solutions of molybdenum trioxide and molybdenum blue. It should be pointed out, however, that any apparent solution which will pass through the finest ultrafilter is not *necessarily* in true solution.

HYDROUS MOLYBDENUM DIOXIDE

Although molybdenum dioxide can be prepared by oxidizing molybdenum or by reducing molybdenum trioxide under suitable

[38] J. Phys. Chem., 29, 966 (1925).

conditions, it is claimed that the hydrous oxide or hydroxide of tetra-valent molybdenum does not exist, the reported preparations being hydrous pentoxide.[39] Jakób and Michalewicz,[40] however, claim to get it as a gel, red-brown in transmitted light and green-brown in reflected light, by the action of alkali on a complex cyanide of tetra-valent molybdenum. The gel analyzed for $MoO_2 \cdot 4H_2O$ after wash-ing with alcohol and ether, but this does not establish it as a hydrate. Paal[41] likewise claims to have prepared the dioxide in a hydrous con-dition by reduction of ammonium molybdate with hydrogen in the presence of colloidal platinum. After using up the theoretical amount of hydrogen, a greenish black mass was obtained which adsorbed all the colloidal platinum. By drying properly, the composition can be made to approximate $MoO(OH)_2$, but there is no evidence that this is a hydrate or that all the molybdenum is tetravalent. If the reduc-tion is carried out in the presence of sodium protalbinate a stable sol is obtained which is black in reflected light and reddish brown in transmitted light.

By a similar procedure, Paal claims to get the precipitated hydrous oxide and sol of trivalent molybdenum.

HYDROUS TUNGSTEN TRIOXIDE AND ITS HYDRATES

PRECIPITATED TUNGSTEN TRIOXIDE

Anhydrous tungsten trioxide does not combine with water, but an insoluble monohydrate usually known as tungstic acid, H_2WO_4, is formed by precipitating a solution of a tungstate with excess mineral acid at the boiling point. The hydrate comes down as a slightly hydrous, yellow powder possessing a definite crystalline structure. The velocity of precipitation and the nature, if not the composition, of the precipitate depend on the hydrogen ion concentration of the solution from which it separates.[42] Hüttig and Kurre[43] dissolved the yellow monohydrate in ammonia, cooled the solution to 0°, and added hydrochloric acid dropwise with rapid stirring. Under these conditions the oxide comes down as a white voluminous mass that cannot be washed completely free from adsorbed salts. Morley[44]

[39] Klason: Ber., 34, 153 (1901); Guichard: Compt. rend., 143, 744 (1906).

[40] Roczniki Chem., 12, 587 (1932).

[41] Paal: Ber., 47, 2214 (1914); Paal and Büttner: 48, 220 (1915).

· [42] Lottermoser: Kolloid-Z., 15, 145 (1914); cf. van Liempt: Rec. trav. chim., 43, 30 (1924).

[43] Z. anorg. Chem., 122, 44 (1922).

[44] J. Chem. Soc., 1987 (1930); J. Phys. Chem., 36, 1655 (1932).

obtained the white oxide by adding 4.4% ammonium molybdate solution to 1.13 N HCl at a temperature of 16.8° and washing the precipitate with tap water.   Apparently the adsorbed impurities stabilize the white oxide, for, if the precipitate from the ammonium molybdate solution is washed thoroughly by decantation with distilled water, it goes over to a pale yellow powder which contains a little more water than corresponds to $WO_3 \cdot 2H_2O$ when dried to constant weight in the air.[45]

Hüttig and Kurre[43] ran the adsorption isobars of the deep yellow and white preparations, obtaining the curves reproduced in Fig. 54. From these, it appears that the deep yellow oxide is a monohydrate and that the voluminous white compound is a hydrous oxide, the
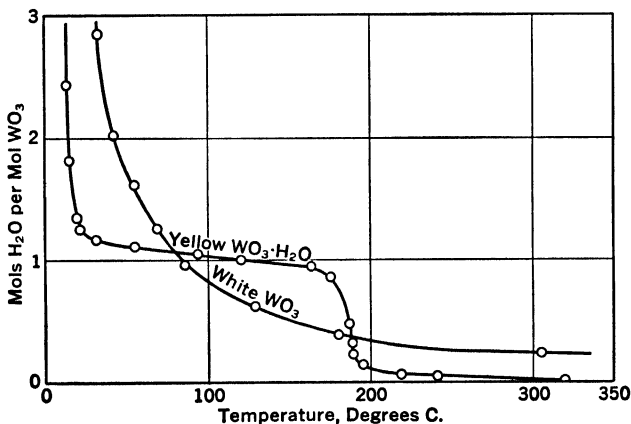
FIG. 54.—Dehydration isobars of yellow and white tungsten trioxides.

water content of which varies continuously with change in temperature.[46]   The curve for the yellow oxide is reproducible; but the ease with which the white compound gives up its water is determined by the size of the hydrous particles.

From x-ray analysis of the several preparations, Morley[47] confirmed Burger's observation that the deep yellow hydrate has a crystalline structure entirely different from that of anhydrous tungsten trioxide.   He showed further that the white oxide gives no definite diffraction pattern and that the lemon-yellow compound which he formulates $WO_3 \cdot 2H_2O$, or preferably $H_2WO_4 \cdot H_2O$, gives a distinctive pat-

[45] Cf. Moser and Ehrlich: Edel-Erden -Erze, **3**, 49, 65 (1922); *also*, Nakazawa and Okada: Elec. Rev., **17**, 89 (1928).

[46] Cf., *also*, Nakazawa and Okada: Elec. Rev., **17**, 89 (1928).

[47] J. Chem. Soc., 1987 (1930).

tern. There is, therefore, no doubt about the chemical individuality of the lemon-yellow compound; but Morley did not run the dehydra-tion isobar and so did not settle definitely whether the compound is a dihydrate or a second crystalline modification of hydrous tungsten trioxide. Burger[3] claims that the white oxide analyzes for $WO_3 \cdot 2H_2O$ and gives a definite x-ray diffraction pattern. He was probably talk-ing about what Morley calls the lemon-yellow hydrate, which seems to be different from the white preparation, although this difference could be one of particle size. The lemon-yellow structure is instable and goes over to the deep yellow monohydrate on aging.

In addition to the above preparations, Morley obtained a mixed product by precipitation at the boiling point when the acidity was less than 0.6 N. It contained, in addition to deep yellow H_2WO_4, a white constituent which turned pale green on drying and gave a dis-tinctive x-ray diffraction pattern. The yellow monohydrate some-times takes on a greenish color especially on ignition, but this has been traced to the formation of a lower oxide, possibly W_2O_5,[48] as a result of a small amount of some reducing impurity in the prepara-tion.[49]

A tungstic acid jelly is obtained by adding 4.5–15 N mineral acid to 3–10% sodium tungstate solution until the acid concentration of the mixture is between 0.1 and 0.5 N, and allowing to stand. The homogeneous jelly can be broken up, washed, and activated like silica gel to make it into a technical adsorbent.[50]

<div align="center">TUNGSTEN TRIOXIDE SOL</div>

The Graham Sol

Graham first prepared a sol of tungsten trioxide or tungstic acid, as he called it, by dialysis of a 5% solution of sodium tungstate acidi-fied with only a slight excess of dilute hydrochloric acid. On evaporat-ing the sol to dryness, a glassy mass was obtained which could be heated to 200° without losing its sol-forming property. An 80% sol with a density of 3.25 was obtained by peptizing the glassy mass with one-fourth its weight of water. The sol is less stable than the corre-sponding molybdenum trioxide sol and precipitates out in the form of beautiful quadratic prisms,[51] after standing several months.

[48] Van Liempt: Z. anorg. Chem., **119**, 310 (1921).

[49] Brinton and Lohmann: Chem. News, **133**, 275 (1926); *cf., however*, Smith and Lukens: **132**, 33 (1925).

[50] Silica Gel Corporation, German Pat. 491,680 (1922); U. S. Pat. 1,683,695; 1,772,055 (1927); 1,848,266 (1929).

[51] Wöhler and Engels: Kolloid-Beihefte, **1**, 472 (1910).

Since the Graham sol cannot be prepared free from alkali, Sabane-jew[52] concluded that it is a solution of sodium salt of the formula $Na_2O \cdot 4WO_3$, sodium metatungstate. This seems not to be the case, since Biltz and Vegesack[53] found the ratio $Na_2O : WO_3$ to be 2 : 11 in a well-dialyzed sol. Moreover, Britton and German[54] obtained sodium tungstate solution in which the ratio $Na_2O : WO_3$ was 1 : 5; and both Ullik[55] and Leontovich[56] prepared sols in which the ratio was 1 : 6 and 1 : 8, respectively. Dumanskii and Buntin[57] representsd the sol as a complex of the general formula $Na_2[WO_4 \cdot nWO_3]$. Diyach-kovskii[58] showed that solutions in which the $Na_2O : WO_3$ ratio was between 2 and 4 were optically clear; solutions in which the ratio was 5 and 6 showed the Tyndall cone in the ultramicroscope and 0.1 N KCl had no effect on them; and solutions in which the ratio was 8 became opalescent at once and precipitated out in a short time.

Unlike colloidal molybdenum trioxide, the Graham sol is not pre-cipitated by adding gelatin,[51] but an adsorption complex is formed which is thrown down by the addition of a little ammonium chloride. The presence of a small amount of tungsten trioxide in colloidal molyb-denum trioxide seems to act as a protecting colloid,[59] preventing the precipitation of the latter by gelatin. Similarly, molybdenum trioxide seems to exert a protecting action on tungsten trioxide. As has been pointed out, molybdenum trioxide comes down only very slowly from a strongly acidified molybdate solution in the cold, whereas tungsten trioxide precipitates readily from a strongly acidified tungstate. If a mixture containing a small amount of tungstate and a large amount of molybdate is acidified, no precipitate forms for a long time unless the mixture is warmed, the time required for its appearance at a given temperature being determined by the composition of the mixture. The precipitate is an adsorption complex since the two oxides exhibit a mutual adsorption for each other. The more stable molybdenum trioxide sol adsorbs and so holds tungsten trioxide in colloidal solution until the particles of the latter grow to the point of precipitation, carrying down with them adsorbed molybdenum trioxide.

[52] Z. anorg. Chem., **14**, 354 (1897).
[53] Z. physik. Chem., **68**, 376 (1910).
[54] J. Chem. Soc., 1249 (1930); 709 (1931).
[55] J. prakt. Chem., **103**, 147 (1868).
[56] J. Russ. Phys.-Chem. Soc., **37**, 130 (1905).
[57] J. Russ. Phys.-Chem. Soc., **58**, 107 (1926).
[58] J. Russ. Phys.-Chem. Soc., **61**, 423 (1929).
[59] *Cf.* Kröger: Kolloid-Z., **30**, 18 (1922).

Sols by Peptization of the Oxide

Although Graham's dialyzed preparations may be solutions of definite salts some of which give colloida' anions, there can be no doubt as to the colloidal character of the preparations formed by mechanical disintegration[60] of the yellow oxide or by washing of the gelatinous oxide. It will be recalled that Lottermoser[61] peptized the voluminous white gel thrown down in the cold by acidifying alkali tungstate. On washing by decantation, preferably by the aid of the centrifuge,[62] the gel becomes less voluminous, light yellow in color, and finally is peptized completely, forming a cloudy sol in which the particles appear rod-shaped.[63] On standing, tactosols similar to those of vanadium pentoxide settled toward the bottom of the container.[62] Lottermoser compares Graham's clear stable sol with the latter's clear ferric oxide sol formed in a similar way, and the cloudy tungsten trioxide sol with Péan de St. Gilles' ferric oxide sol. This comparison is not justified, since both ferric oxide sols are colloidal α-Fe_2O_3, differing only in the size and hydrous character of the particles, whereas the two tungsten trioxide sols are different chemically.

Kargin[64] modified Lottermoser's procedure by washing the precipitated oxide with hydrochloric acid to remove any sodium as sodium chloride before peptizing by washing and dialyzing. This sol was quite sensitive to the action of electrolytes, and the displacement of H^+ ions during the coagulation process was followed potentiometrically. Just as with arsenic trisulfide sol,[65] the adsorption of cations such as silver[66] during coagulation is greater than that of the hydrogen displaced. The explanation of this general behavior has been considered in detail in earlier chapters (pp. 73 and 114). The hydrophobic character of the negative sol formed by peptization is well illustrated by the following precipitation values of several electrolytes, in millimols per liter:[67] LiCl, 170; NaCl, 23.1; KCl, 7.41; $K_3Fe(CN)_6$, 8.68; CsCl, 2.44; $Be(NO_3)_2$, 2.44; $CaCl_2$, 0.83; $BaCl_2$, 0.65; $AlCl_3$, 0.43.

Pappadà[68] prepared a very sensitive sol by peptizing the precipi-

[60] Wegelin: Kolloid-Z., **14**, 65 (1914).
[61] Van Bemmelen's "Gedenkboek," 152 (1910); Kolloid-Z., **15**, 145 (1914).
[62] Zocher and Jacobsohn: Kolloid-Beihefte, **28**, 167 (1929).
[63] Diesselhorst and Freundlich: Physik. Z., **17**, 117 (1916).
[64] Kolloid-Z., **49**, 281 (1929).
[65] Weiser and Gray: J. Phys. Chem., **36**, 2796 (1932).
[66] Rabinovich and Avtonomova: Kolloid-Z., **55**, 207 (1931).
[67] Cf., also, Ghosh and Dhar: J. Phys. Chem., **33**, 1906 (1929).
[68] Gazz. chim. ital., **32** II, 22 (1902).

tated oxide with oxalic acid and purifying by dialysis; and Müller[69] obtained a sol highly sensitive to electrolytes by diluting with water an alcohol-ether solution of the oxide formed by the hydrolysis of $WOCl_4$. The negative sol resulting from peptization of the precipitated gel with an acid or base is more hydrophilic in character, but it is coagulated even by salts with univalent cations.[70]

TUNGSTEN BLUE

The first product formed on reducing tungsten trioxide or a tungstate is a blue substance similar to molybdenum blue and known as tungsten blue. It may be formed also by partial oxidation of tungsten dioxide or of the hydrolysis product of tungsten pentachloride or pentabromide. The composition of the blue has been represented by a number of formulas ranging from W_2O_5[71] to W_5O_{14};[72] but the bulk of the evidence indicates that it is a mixture of variable composition and not a single chemical individual.[73] Depending on the method of preparation, the color varies from purple-bronze to deep blue, but it is not known whether this is due to difference in composition or physical structure or both. Tarjan[74] prepared definite red-violet, triclinic needles with a metallic luster which analyzed for W_4O_{11}.

A sol of tungsten blue is formed by neutralization with ammonia of a solution of metatungstic acid saturated with hydrogen sulfide,[75] or by electrolytic reduction of an acidified tungstate solution.[76] In the purification by dialysis, appreciable amounts of the blue substance pass through the dialyzing membrane; the sol remaining has a deep sky-blue color in marked contrast to the slate-blue color of the corresponding molybdenum sol. Like the latter, however, it is negatively charged and is precipitated by electrolytes and positively charged sols. Freshly prepared sols dye silk, cotton, and wool directly, imparting a clear blue color to the fiber.[77]

[69] Kolloid-Z., **8**, 93 (1911).

[70] Normand and Muthanna: Proc. 15th Indian Sci. Cong., 137 (1928).

[71] Chaudron: Compt. rend., **170**, 1056 (1920); Ann. chim. (10) **16**, 221 (1921); van Liempt: Z. anorg. Chem., **126**, 183 (1923).

[72] Allen and Gottschalk: Am. Chem. J., **27**, 328 (1902).

[73] Wöhler and Balz: Z. Elektrochem., **27**, 406 (1921); Wöhler, Shibata, and Kunst: **38**, 808 (1932); Reinders and Vervloet: Rec. trav. chim., **42**, 625 (1923).

[74] Naturwissenschaften, **19**, 166 (1931).

[75] Scheibler: J. prakt. Chem., **80**, 204 (1860); **83**, 273 (1861); Biltz: Ber., **37**, 1095 (1904).

[76] Leiser: Z. Elektrochem., **13**, 690 (1907); Kröger: Kolloid-Z., **30**, 16 (1922).

[77] Biltz: Ber., **37**, 1771 (1904).

HYDROUS URANIUM TRIOXIDE HYDRATE

Graham[78] first prepared a sol of uranium trioxide by adding potassium carbonate to a uranyl salt solution containing sugar, and dialyzing. The deep orange-yellow colloid was very stable but was readily agglomerated by electrolytes. It is not clear why Graham found it necessary to use sugar in the preparation of his sol, for Szilard[79] found that uranyl nitrate peptizes the oxide directly. To get the oxide in suitable form, Szilard mixed a solution of uranyl acetate with ether and exposed the mixture to light, thereby obtaining a hydrous violet precipitate[80] analogous to molybdenum blue but having a definite composition U_3O_8. On allowing the thoroughly washed oxide to stand for a day, it oxidized to the yellow trioxide which was suspended in water and added to a hot solution of uranyl nitrate as long as it was peptized easily. The orange-yellow sol was quite stable in the presence of an appreciable excess of uranyl salt; but if too much oxide was added, it agglomerated spontaneously in a form that was not readily repeptized.

It is altogether probable that the sol is a hydrate rather than a hydrous oxide, since the anhydrous oxide takes up water at room temperature,[81] forming a dihydrate that is converted into a monohydrate at a temperature of 80° and a water-vapor pressure of 15 mm.[82] The hydrate is usually yellow in color, but an orange compound of the same composition is obtained by electrolysis of uranyl nitrate[83] or by suspending the violet hydrous U_3O_8 in water which is subsequently boiled in the air.[84] The anhydrous oxide formed by decomposition of uranyl nitrate is yellow if the decomposition takes place slowly, but red if the decomposition is rapid.[85] It is probable that the variations in color of both the anhydrous and hydrated oxides are the result of differences in physical character of the same compound formed in different ways.

It is of particular interest that colloidal uranium trioxide appears

[78] Phil. Trans., **151**, 183 (1861).

[79] J. chim. phys. (2) **5**, 488, 495, 636 (1907).

[80] Aloy: Bull. soc. chim. (3) **25**, 344 (1901); Aloy and Rodier: (4) **27**, 101 (1920).

[81] Lebeau: Compt. rend., **154**, 1808 (1912).

[82] Hüttig and Schroeder: Z. anorg. Chem., **121**, 243 (1922).

[83] Oechsner de Coninck: Bull. acad. roy. med. Belg., **3**, 222 (1901).

[84] Oechsner de Coninck: Compt. rend., **132**, 204 (1901); Bull. acad. roy. med. Belg., 363, 448 (1904).

[85] Aloy: Bull. soc. chim. (3) **23**, 368 (1900).

to catalyze the formation of formaldehyde by the action of sunlight on a solution of carbon dioxide in water.[86]

HYDROUS URANIUM DIOXIDE

Hydrous uranium dioxide is thrown down as a voluminous, red-brown mass by adding alkalis or ammonia to a cold green uranous solution.[87]   The gel loses water and becomes denser and darker on heating.   It is probable that the newly formed hydrous mass would be peptized by washing, since Samsonow[88] obtained a sol by washing the dark hydrous dioxide precipitated during the electrolytic reduction of 50 g of uranyl chloride in 100 cc of 2 N HCl.   Samsonow's sols, when freshly prepared, contained small positively charged particles in brisk Brownian movement.   The particles grew quite rapidly, however, and within 24 hours most of the oxide settled out.

[86] Moore and Webster: Proc. Roy. Soc. (London) 87B, 163 (1913); 90B, 168 (1919).

[87] Aloy: Bull. soc. chim. (3) 21, 613 (1899).

[88] Kolloid-Z., 8, 96 (1911).

CHAPTER XIII

THE HYDROUS OXIDES OF MANGANESE

Four oxides of manganese can be prepared in a more or less hydrous state. Since the dioxide has been studied most extensively it will be considered first.

HYDROUS MANGANESE DIOXIDE

PRECIPITATED MANGANESE DIOXIDE

Formation

Hydrous manganese dioxide is obtained by the oxidation of manganous salts with such oxidizing agents as permanganate, hypochlorite, chlorate, ammonium persulfate, nitric acid, and ozone. It is also obtained by hydrolysis of a salt of tetravalent manganese and by reduction of permanganate by hydrogen peroxide, glycerol, dextrose, potassium oxalate, etc. It is difficult, if not impossible, to obtain the hydrous oxide in a pure form, partly on account of its tendency to lose a portion of its oxygen, giving mixtures of MnO and MnO_2,[1] and partly because of its high adsorption capacity.

Composition

Manganese dioxide is said to form hydrates such as $MnO_2 \cdot 0.5H_2O$ and $MnO_2 \cdot H_2O$[2] but this seems unlikely in the light of van Bemmelen's[3] observation that the composition is indefinite, depending on the physical character, age, and conditions of drying the precipitate. Van Bemmelen worked with two different samples; one the ordinary dark brown or black compound thrown down from a manganous salt solution with alkali hypochlorite, and the other a so-called red variety obtained by hydrolysis of $Mn(SO_4)_2$.[4] The latter preparation is not really red but possesses a brown color when thoroughly dried.

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[1] Wright and Menke: J. Chem. Soc., **37**, 25 (1880); Gooch and Austin: Am. J. Sci. (4) **5**, 260 (1898); Gorgeu: Compt. rend., **110**, 1134 (1890); Knorre: Z. angew. Chem., **14**, 1149 (1901).

[2] Meyer and Kanters: Z. anorg. Chem., **185**, 178 (1929).

[3] J. prakt. Chem. (2) **23**, 324, 379 (1881).

[4] Fremy: Compt. rend., **82**, 475, 1231 (1876).

It is more finely divided than the black precipitate and possesses a higher adsorption capacity for water and dissolved electrolytes.

Simon and Feher[5] confirmed van Bemmelen's conclusion that manganese dioxide forms no hydrates, by means of temperature-composition curves for different precipitates obtained in the following ways: (1) action of NH_4OH and Br_2 on 8% $MnCl_2$ at room temperature (reddish brown); (2) action of $(NH_4)_2S_2O_8$ on 8% $MnCl_2$ (dark brown to black); (3) action of dilute $(NH_4)_2S_2O_8$ on 3% $MnCl_2$ (black, metallic); (4) hydrolysis of K_2MnCl_6[6] (clear brown, very voluminous); (5) hydrolysis of Na_2MnO_3[7] at the boiling point (reddish brown). After washing the several preparations with alcohol and ether the isobars were obtained of which the three reproduced in Fig. 55 are typical.
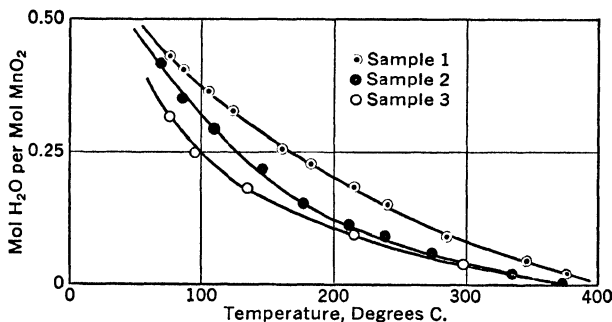
FIG. 55.—Dehydration isobars of hydrous manganese dioxides.

Adsorption

Hydrous manganese dioxides show a strong tendency to adsorb hydroxyl ion as evidenced by the fact that dilute solutions of alkali peptize the freshly formed gel, giving a stable negative sol.   Solutions of neutral salts take on an acid reaction in contact with manganese dioxide.[8]   This may be due to hydrolytic adsorption (Vol. I, p. 292) in which more base than acid is adsorbed, or it may result from an exchange adsorption.   The latter seems the more probable in the light of the observations of Mukherjee[9] and Ghosh.[10]   Like silica, manganese dioxide is negatively charged in contact with water.   Since the

[5] Kolloid-Z., 54, 49 (1931); Hebler: Farben-Ztg., 31, 155; Wilborn: 338 (1925).

[6] Weinland and Dinkelacker: Z. anorg. Chem., 60, 173 (1908).

[7] Grube and Metzger: Z. Elektrochem., 29, 17 (1923).

[8] Van Bemmelen: J. prakt. Chem. (2) 23, 324, 379 (1881); Gorgeu: Ann. chim. phys. (3) 66, 155 (1862); Hümmelchen and Kappen: Z. Pflanzenernähr. Düngung, 3A, 289 (1924); Beling: Kolloid-Beihefte, 35, 265 (1932).

[9] Phil. Mag. (6) 44, 321 (1922).

[10] J. Chem. Soc., 2605 (1926).

oxide possesses such weak acid properties, any acids it may form will probably be condensation products of indefinite composition that may be represented by $H_2Mn_nO_{(2n+1)}$.[11] The negative charge on the hydrous particles would result from preferential adsorption of the complex anion, $HMn_nO_{(2n+1)}{}^-$, which would become the inner portion of the double layer, with H^+ constituting the diffuse outer portion. On bringing the oxide in contact with a neutral salt solution, the cations will be adsorbed, displacing H^+ ions and giving the solution an acid reaction. Since the adsorption of simple cations by a negatively charged surface is determined by their valence, mobility, and hydration, one would predict simple cations to be adsorbed in the order: Ba > Sr > Ca > K > Na > Li, and the capacity to liberate hydrogen to be in the same order. This is in entire agreement with the observations of Ghosh.[12] Moreover, the latter noted that the adsorption of the divalent cations reversed the surface charge and that the adsorption of one barium ion displaced but a single hydrogen ion. This suggests that the point charges constituting the primary sheet of the double layer are univalent ions [OH^- or $HMn_nO_{(2n+1)}{}^-$], and that, when one divalent ion is fixed on any of these point charges, its corresponding hydrogen ion is displaced and the surface at this point has a net positive charge.

If one attempts to explain the above phenomena on purely chemical grounds, it would be necessary to assume that the s o l u b i l i t y of the series of complex salts will be in the order: Ba < Sr < Mg and K < Na < Li. It is not possible to predict this *a priori*; nor does the charge reversal follow from such considerations.

FIG. 56.—Adsorption of $BaCl_2$ by hydrous MnO_2 (results of 7 experiments).

The adsorption of barium chloride by hydrous manganese dioxide is shown in Fig. 56 from Chlopin and Balandin.[13] They con-

[11] Cocosinschi: Z. anorg. Chem., **186**, 176 (1930).

[12] *Cf.*, *also*, Mukherjee, Roychoudhury, and Rao: J. Indian Chem. Soc., **7**, 803 (1930).

[13] Z. anorg. Chem., **149**, 157 (1925); *cf.* Vol. 1, p. 187.

sider that the process involves the following chemical reaction: $MnO_2 \cdot H_2O + BaCl_2 = BaMnO_3 + 2HCl$, giving $2H^+$ for each Ba^{++} taken up in accord with the mass law. Actually, the solution after adsorption contains less hydrochloric acid than corresponds to the barium adsorbed;[14] but this is attributed to adsorption of molecular hydrochloric acid and barium chloride. This mechanism would seem to be much less satisfactory than the exchange adsorption mechanism. Since it is necessary to assume molecular adsorption to account for a part of the observed behavior, nothing is gained by attempting to picture the phenomenon as a chemical process of the ordinary type. Certainly, to assume the existence of $MnO_2 \cdot H_2O$ goes well beyond the known facts. Pavlov[15] likewise does not help matters when he assumes that the adsorption of silver nitrate by hydrous manganese dioxide is an ordinary chemical process involving the formation of basic salts of indefinite composition.

The adsorption by manganese dioxide from solutions containing such ions as Fe^{+++}, Ni^{++}, and Cu^{++} follows the Freundlich adsorption isotherm, the amounts of the several cations taken up being proportionately greater at lower concentrations.[16] A study of the simultaneous adsorption of binary mixtures of ions such as $Fe^{+++}-Ni^{++}$, $Cu^{++}-Ni^{++}$, $Fe^{+++}-Cu^{++}$, and $Mn^{++}-Cu^{++}$ disclosed[17] that the Freundlich equation, $x/m = kC^{1/n}$ or $a = kC^{1/n}$, holds for either one of the two ions provided the concentration of the other is kept constant. The constants k and n were found to be functions of the equilibrium concentration of the ion which varies in amount. In other words, in simultaneous adsorption, the adsorption of one ion cuts down the adsorption of the other but the relative distribution of either ion between the solid and liquid phase is not affected by the presence of the other.

Radium is adsorbed selectively from radium-barium solutions to a greater extent by hydrous manganese dioxide than by hydrous silica.[18] The radium is recovered by dissolving the product in hydrochloric acid and passing in hydrogen chloride to precipitate the chloride. Puilkov[19]

[14] *Cf.* Chakravarti and Dhar: J. Phys. Chem., **2**, 997 (1927).

[15] Kolloid-Z., **35**, 375 (1924).

[16] Geloso: Compt. rend., **176**, 1884 (1923); **178**, 1001 (1924); Bull. soc. chim. (4) **37**, 641 (1925); Ann. chim. (10) **6**, 352; **7**, 113 (1927).

[17] Geloso and Levy: Compt. rend., **186**, 35; Levy: 1619 (1928); **192**, 1376 (1931); Ann. chim. (10) **15**, 85 (1931); *cf.* Mehrotra and Sen: J. Indian Chem. Soc., **3**, 297 (1926).

[18] Ebler and Bender: Z. anorg. Chem., **84**, 77 (1913).

[19] J. Gen. Chem. (U.S.S.R.) **1**, 589 (1931).

showed that the hydrous oxide exhibits a marked selective adsorption capacity for ionium and germanium.

Manganese dioxide alone or mixed with other oxides is a good catalyst for the oxidation of carbon monoxide, and it has been used rather extensively in adsorption studies.   An active oxide is obtained by sifting finely powdered potassium permanganate into concentrated nitric acid, washing the resulting oxide, and drying at 110–115°.[20]   A pure active oxide is also obtained by passing ozone through a neutral solution of manganous acetate or by electrolysis of manganous nitrate with the anode surrounded by a porous cup.[21]   .

The adsorption isotherms for vapors such as water and benzene were found by Foote and Dixson[22] to consist of two parts due to (1) surface adsorption and (2) condensation of the vapor on the surface. The data are in accord with Polanyi's theory which postulates surface adsorption followed by liquefaction of the adsorbed vapor.   The adsorption of water vapor is a purely surface phenomenon when the pressure is less than two-fifths of the saturation value.   Water vapor cuts down the adsorption of carbon dioxide, carbon monoxide, and oxygen; hence it retards the catalytic oxidation of carbon monoxide. Adsorption on mixed copper oxide-manganese dioxide catalysts has been studied extensively by Bray and his students.[23]

The molecular and activated adsorption of hydrogen and carbon monoxide on manganous oxide catalyst has been considered in Vol. I, page 199.

MANGANESE DIOXIDE SOL

Formation without Organic Protecting Agents

As already noted, van Bemmelen observed the ease with which hydrous manganese dioxide is peptized by dilute alkali.   He also noted that the most hydrous oxides are more or less completely peptized by washing out the excess of adsorbed alkali or salt,[24] forming clear brown sols that are quite sensitive to the action of electrolytes.

The most satisfactory method of preparing the sol consists in reducing potassium permanganate under such conditions that the

[20] Whitesell and Frazer: J. Am. Chem. Soc., **45**, 2841 (1923).

[21] Meloche and Weiner: J. Am. Chem. Soc., **56**, 1645 (1934).

[22] J. Am. Chem. Soc., **52**, 2170 (1930); **53**, 55 (1931); cf. Lanning: **52**, 2411 (1930).

[23] Almquist and Bray: J. Am. Chem. Soc., **45**, 2305 (1923); Hoskins and Bray: **48**, 1454; Bray and Doss: 2060 (1926); Draper: **50**, 2637 (1928).

[24] Cf., also, Gorgeu: Ann. chim. phys. (3) **66**, 154 (1862); Spring: Ber., **16**, 1142 (1883); Spring and De Boeck: Bull. soc. chim. (2) **48**, 170 (1887).

precipitation concentration of no electrolyte in the solution is exceeded. The solution becomes alkaline during the reductions, but as we have seen, an appreciable concentration of hydroxyl ion is favorable to sol formation. Reducing agents that have been employed successfully are hydrogen peroxide, sodium thiosulfate, arsenious acid, reducing sugars, ammonia, and acetylene.

Swiontkowski[25] first reported the formation of a coffee-colored sol of manganese dioxide by reducing a solution of potassium permanganate with pure neutral hydrogen peroxide. According to Bredig and Marck,[26] a satisfactory sol results if a dilute hydrogen peroxide solution is added slowly with constant shaking to a potassium permanganate solution no stronger than $M/10$, until the color of the permanganate just disappears. By dialysis with conductivity water, the conductivity of the sol may be reduced to that of ordinary distilled water. A dilute sol is clear yellow in color, changing to dark brown as the concentration increases. If not too concentrated, the sol can be kept indefinitely without precipitating; but it is very sensitive to the action of electrolytes with the exception of potassium hydroxide and permanganate.

The reduction of permanganate by arsenious acid was shown by Deisz[27] to give a very stable sol, particularly if it is not subjected to dialysis. If evaporated to dryness over sulfuric acid, a residue is obtained which is again converted into a sol by shaking with water. If a bit of sol is allowed to drop into still water, beautiful vortex rings are formed. The first ring increases to a certain size and breaks into several small rings, and these in turn into others. All these rings are connected with each other by thin lines of hydrous manganese dioxide, thus giving the whole system a striking clustered or festooned appearance. If the sol is dropped into a salt solution, it is precipitated in the form of miniature rings; by using a very dilute solution, the system of rings will form before coagulation takes place. This phenomenon, first described by Thomson and Newall,[28] is not limited to colloids like milk, ink, blood, soap, etc., but is shown by many solutions of both electrolytes and non-electrolytes. Suitable concentrations of permanganate give strikingly beautiful rings.

Probably the simplest method of preparing manganese dioxide sol consists in adding concentrated ammonia, one drop every 3 minutes,

[25] Ann., **141**, 205 (1867).
[26] Van Bemmelen's "Gedenkboek," 342 (1910).
[27] Kolloid-Z., **6**, 69 (1910); cf. Travers: Bull. soc. chim. (4) **37**, 456 (1925).
[28] Proc. Roy. Soc. (London) **39**, 417 (1886).

to $M/20$ KMnO$_4$ at 90° until all the permanganate is reduced.[29]   The only impurity in the sol is potassium hydroxide, which has a marked stabilizing effect.   The purification of the sol by dialysis is attended with some difficulty since it coagulates in contact with parchment paper.   Joshi and Narayan[30] got around this in two ways: (1) by applying a negative potential of 200 volts to the membrane, and (2) by hot dialysis.   The coagulating action is due to adsorption by the membrane, and this is cut down by giving the membrane a negative charge or by raising the temperature.   The almost electrolyte-free sols prepared in this way are very sensitive toward electrolytes.

The reduction of dilute solutions of permanganate with ethylene[31] yields fairly satisfactory sols since the products of the reaction, potassium hydroxide and glycol, exert a stabilizing action.   The sol formed by reduction with acetylene is instable unless a small amount of colloidal silica is present.[31]

Formation with Organic Protecting Agents

Witzemann[32] prepared colloidal manganese dioxide by incomplete oxidation of a glucose solution in the presence of a little alkali.   On adding slowly 100 cc. of 6% KMnO$_4$ to a cold solution containing 5 g of glucose in 20 cc, together with a few cubic centimeters of 10% NaOH, the mixture rapidly became viscous and set to a stiff jelly in 5 to 10 minutes.   The jelly soon started to synerize, and after standing for a few days it was transformed completely into a stable, limpid sol.   The rate of transformation from the jelly to the sol stage depends on the alkali concentration.   With quite low concentrations, the jelly forms slowly and does not liquefy; whereas with relatively high concentrations, the jelly stage is not observed, the solutions merely undergoing an initial increase in viscosity, followed by a rapid transformation to the limpid sol.   This behavior of colloidal manganese dioxide is very similar to that of colloidal hydrous ceric oxide[33] except that in the latter case the transformation from a hydrous sol to a jelly, and again to a less hydrous sol, takes place in the absence of glucose.   It is obvious that the newly formed particles of manganese dioxide are in an extremely finely divided and highly hydrous form; and in relatively

[29] Cuy: J. Phys. Chem., **25**, 415 (1921); *cf., however*, Chirnoaga: Kolloid-Z., **68**, 298 (1934).

[30] J. Indian Chem. Soc., **7**, 883 (1930).

[31] Steopoe: Kolloid-Z., **39**, 35 (1926); Bull. soc. romana stiinte, **29**, 11 (1926).

[32] J. Am. Chem. Soc., **37**, 1079 (1915); **39**, 27 (1917).

[33] Kruyt and van der Made: Rec. trav. chim. (4) **42**, 277 (1923).

high concentration, they adsorb and entangle all the liquid, forming a jelly. Many inorganic jellies synerize, particularly in the presence of salts, the hydrous particles losing water and growing until they settle out. This is particularly noticeable with barium sulfate and certain arsenate jellies. But, in hydrous manganese dioxide, the primary particles coalesce to form larger primary particles even though agglomeration and precipitation are prevented by the protective action of glucose and the peptizing action of adsorbed hydroxyl ion. The aging of the primary particles in the presence of electrolytes has, however, left them relatively free from adsorbed water, which merely serves as the medium in which the slightly hydrous particles are suspended. Because of this irreversible change, neither an aged ceric oxide nor manganese dioxide sol can be precipitated in the form of a jelly. As we have seen, jellies of the hydrous oxides of iron and aluminum may be broken up by shaking, forming sols of relatively low viscosity which, on standing, set again to firm jellies. In these instances the primary particles retain their small, highly hydrous character in contradistinction to the behavior of ceric oxide and manganese dioxide, and the structure broken up by shaking gradually re-forms, entangling all the unadsorbed water (*cf.* p. 23).

A stable sol may be obtained by the oxidation of manganous salt in the presence of a protecting colloid,[34] such as albumin, dextrin, gum arabic, sodium "salts" of albuminous products, and starch. Low concentrations of positive ferric oxide sol precipitate negative manganese dioxide sol, but sufficiently high concentrations adsorb it completely and hold it in the suspended form. Thus, a dark brown hydrosol is obtained by dissolving a manganous salt in a neutralized ferric chloride solution and treating with potassium permanganate; similarly, a ferrous chloride solution can be oxidized with a potassium permanganate solution without precipitation taking place.

Stability

The negatively charged sol is relatively instable when quite pure; hence, most preparations with which people have worked have not been purified. This probably accounts for certain abnormalities in the observed order of precipitating power of cations by the sol and the order of their adsorption during the coagulation process.[35] With a

[34] Trillat: Compt. rend., **138**, 274 (1904); Bull. soc. chim. (3) **31**, 811 (1904); Heyden: German Pat. 227,491 (1909).

[35] Ganguly and Dhar: J. Phys. Chem., **26**, 701, 836 (1922); Dhar, Sen, and Ghosh: **28**, 457 (1924); Chakravarti and Dhar: **31**, 997 (1927); Chatterji and Dhar: Kolloid-Z., **33**, 18 (1923); Steopoe: Bull. soc. romana stiinte, **29**, 11 (1926).

pure sol, Hazel and McQueen[36] found the effectiveness of cations in decreasing the mobility of the particles to be: Th > Al > Cr, Fe > Ba > K, which is usual with negative sols.   Moreover, the pure sol behaves normally in the mutual coagulation process with other sols.[37]

Catalytic Action

Colloidal manganese dioxide catalyzes the decomposition of hydrogen peroxide (Vol. I, p. 239).   The process has been studied quantitatively by Bredig and Marck.[38]   The reaction is of the first order, but in most cases the constant increases as the decomposition progresses, possibly owing to the formation and subsequent decomposition of a hydrogen peroxide salt during the course of the reaction.[39] In alkaline solution, the velocity of decomposition increases to a maximum with increasing concentration of hydroxyl ion and then falls off just as Bredig found with colloidal metals.   The catalytic activity of the oxide is increased by heating the sol for one-half hour, but prolonged heating causes precipitation.   The presence of gelatin increases the stability of the sol and raises the catalytic activity slightly.   Low concentrations of substances like hydrogen sulfide, potassium cyanide, and carbon dioxide, which have a marked poisoning action on a platinum catalyst, are without effect on manganese dioxide.   On the other hand, phosphorus, its oxidation products, and sodium phosphate cut down the catalytic activity of the oxide, and mercuric chloride and potassium fluoride increase it.

A mixture of perborate and permanganate may be added to bath water to make what is known as an "oxygen bath."   The reaction in solution gives hydrogen peroxide and colloidal manganese dioxide, and the latter catalyzes the decomposition of the former, setting free oxygen which forms a supersaturated solution in the water and is subsequently evolved in small bubbles on the skin of the bather. The presence of electrolytes in the bath water was found to have such a marked effect on the rate of evolution of oxygen that Lottermoser[40] investigated quantitatively the influence of various alkalis and salts on the decomposition of hydrogen peroxide by manganese dioxide. The impurity was added to the peroxide solution, after which the

[36] J. Phys. Chem., 37, 559 (1933).
[37] Hazel and McQueen: J. Phys. Chem., 37, 577 (1933); Simakov: Kolloid-Z., 45, 207 (1928).
[38] Van Bemmelen's "Gedenkboek," 342 (1910).
[39] Cf., however, Lottermoser and Lehmann: Kolloid-Z., 29, 250 (1921).
[40] Lottermoser and Lehmann: Kolloid-Z., 29, 250 (1921).

catalyst was prepared directly in the solution by adding permanganate and base in the order named. With salts of a common anion, different cations influenced the decomposition in the order: $Ba^{++} >$ $Sr^{++} > Ca^{++} > Na^+ > K^+ > Li^+$, barium ion accelerating it the most and lithium ion retarding it the most. Unfortunately, Lottermoser did not inquire into the reason for the accelerating action of certain electrolytes and the inhibiting action of others; but it is probable that this is very closely related to the adsorbability of the cations and to the variation in physical character of the hydrous particles formed in the presence of different electrolytes. Mg^{++} and NH^+ ions were found to have a marked retarding action by cutting down the concentration of hydroxyl ion. For preparing a satisfactory oxygen bath, it is obviously necessary to avoid waters containing magnesium salts.

Manganese compounds have been found to play an important rôle in many biochemical actions, and in certain instances, this may be due to colloidal oxides of manganese.[41] Thus manganese compounds stimulate alcoholic fermentation[42] and the growth of fungi.[43] The stimulating effect on the growth of plants in general[44] is evidenced by the fact that the production of wheat per acre may be increased 10% by sprinkling a manganese compound on certain soils. For this purpose, manganese dioxide is one of the most effective compounds. Salts of manganese likewise appear to stimulate metabolism and to increase the hemogenetic power.[45] It is therefore proposed to administer manganese therapeutically along with iron to make the iron more effective. Further, the addition of minute amounts of manganese increases the activity of the enzyme laccase,[46] and colloidal manganese dioxide behaves like an oxidase toward guiac tincture, hydroquinone, etc.[47] As the processes mentioned are thought to be regulated by enzymes and enzymes are colloidal, Witzemann sug-

[41] Witzemann: J. Am. Chem. Soc., **37**, 1089 (1915).

[42] Kayser and Marchand: Compt. rend., **145**, 343 (1907).

[43] Bertrand and Javillier: Bull. soc. chim. (4) **11**, 212; Bertrand: 494 (1912); Waterman: J. Chem. Soc., **104**, 229 (1913).

[44] Masoni: Staz. sper. agrar. ital., **44**, 85; Montemartini: 564 (1911); Ricci and Barbera: **48**, 677 (1915); Bartmann: J. agr. prat. (2) **20**, 666 (1911); Skinner and Sullivan: U. S. Dept. Agr. Bull. **42** (1913); Pfeiffer and Blanck: Landw. Vers.-St., **77**, 33 (1912); **83**, 257 (1913).

[45] Piccinini: Eighth Int. Cong. Applied Chem., **19**, 263 (1912); Biochem. terp. sper., **2**, 385 (1910–1911); Chem. Abstracts, **7**, 369 (1913).

[46] Bertrand: Bull. soc. chim. (3) **17**, 619, 753 (1897); Ann. chim. phys. (7) **12**, 115 (1897); cf., also, Bach: Ber., **43**, 364 (1910).

[47] Sjollema: Chem. Weekblad, **6**, 287 (1909); Chem. Zentr., I, 496 (1911).

gests that the effect of manganese on enzymic activity is due to the effect of the hydrous oxide on the physical character of the enzyme. Thus, if the colloidal oxide keeps the colloidal enzyme dispersed under conditions which would normally be unfavorable to this effect, it might be expected'to have a positive influence on the enzymic activity.

OTHER HYDROUS OXIDES OF MANGANESE

Hydrous Manganous Hydroxide. By adding alkali hydroxide to a solution of manganous salt, white manganous hydroxide precipitates in a highly gelatinous form. The hydrous precipitate adsorbs chloride slightly and sulfate strongly, so that the chloride is not carried down in the presence of the sulfate.[48] It can be obtained in regular hexagonal prisms, similar to the mineral pyrochroite,[49] by adding manganous chloride to a boiled concentrated solution of potassium hydroxide in an atmosphere of hydrogen.[50] By heating to 160°, all the hydroxide is carried into solution, from which it precipitates in transparent crystals having a reddish tint. When pure, the crystalline hydroxide is fairly stable in the air; but if it contains even a small amount of alkali, it oxidizes very readily. Like magnesium hydroxide, it dissolves in excess ammonium chloride.[51]

A sol of hydrous MnO or $Mn(OH)_2$ is formed by treating a solution of manganous salt with alkali in the presence of protecting colloids such as gelatin,[52] Paal's "sodium protalbinate,"[53] albumin,[34] and nucleic acid.[54] Because of its fine state of subdivision, it oxidizes readily to MnO_2. In the presence of certain reducing agents, such as hydroquinone and gallic acid, hydrous MnO_2 will give up oxygen, again forming colloidal MnO,[55] the process coming to a standstill only when there is no further reduction to MnO by the reducing agent, that is, when the oxidation of the added substance is complete. This action as an oxidase or oxygen carrier probably accounts for the rapid drying of manganese oxide paints, varnishes, and siccatives. The drying oil, such as linseed, doubtless plays the double rôle of protecting colloid and oxygen-consuming reducing agent.[56]

[48] Patten: J. Am. Chem. Soc., **25**, 192 (1903).
[49] Cf. Natta: Gazz. chim. ital., **58**, 344; Natta and Passerini: 597 (1928).
[50] De Schulten: Compt. rend., **105**, 1265 (1887).
[51] Cf. Herz: Z. anorg. Chem., **21**, 242 (1899); **22**, 279 (1900).
[52] Lobry de Bruyn: Z. physik. Chem., **29**, 562 (1899); Rec. trav. chim., **19**, 236 (1900).
[53] Kalle and Co.: German Pat. 180,729 (1901).
[54] Sarason: German Pat. 272,386 (1913).
[55] Bertrand: Compt. rend., **124**, 1032, 1355; Villiers: 1349 (1897).
[56] Cf. Livache: Compt. rend., **97**, 1311 (1883); **124**, 1520 (1897).

Hydrous Manganic Oxide. Hydrous manganic oxide is best prepared by hydrolysis of manganic salts, but it is also obtained in a more or less pure condition by the partial oxidation of manganous salts. By drying at 100°, the composition is said to be represented by the formula $Mn_2O_3 \cdot H_2O$, corresponding to the mineral manganite;[57] but Hebler[58] considers it to be a typical hydrous oxide with an indefinite amount of water. When formed by the hydrolysis of potassium manganic cyanide, it is a black gelatinous mass which becomes less hydrous on heating with the mother liquor, changing in color from black to brown.[59] Meyer[60] suggests that the color change may be due either to the decomposition of a hydrate or to a change in the size and physical character of the particles; he leaves the matter for someone else to decide.

Anargyros[61] claims to have prepared colloidal manganic oxide by the reduction of potassium permanganate by sodium arsenite at 65 to 70°. The propyl alcosol is obtained by the interaction of propyl alcohol solutions of K_2O and $MnCl_2$ in the presence of air.[62] The sol doubtless contains some manganous oxide.

Hydrous Mangano-manganic Oxide. The oxide Mn_3O_4 or $MnO_2 \cdot 2MnO$ is the most stable of all the oxides of manganese when heated in the air. Accordingly, higher oxides decompose around 940° and lower oxides oxidize in the air, forming Mn_3O_4. It is obtained in a hydrous condition, more or less impure, by treating a mixture of manganous and manganic salts with alkali or by the oxidation of an ammoniacal solution of a manganous salt with oxygen. Christensen[63] obtained it by adding hydrous MnO_2 in small amounts at a time to a dilute solution of manganous chloride containing an excess of ammonium chloride. Depending on the exact condition of formation, the precipitate is yellow-brown, red-brown, or chocolate-brown in color.

[57] Franke: J. prakt. Chem. (2) **36**, 31, 451 (1887); Meyer: Z. anorg. Chem., **81**, 385 (1913).

[58] Farben-Ztg., **31**, 155 (1925).

[59] Berthier: Ann. chim. phys. (2) **20**, 344 (1822); Hermann: Pogg. Ann., **74**, 303 (1848); Gorgeu: Compt. rend., **106**, 748 (1888).

[60] Z. anorg. Chem., **81**, 400 (1913).

[61] Compt. rend., **181**, 419 (1925).

[62] Weiser and Mack: J. Phys. Chem., **36**, 86 (1930).

[63] Z. anorg. Chem., **27**, 321 (1901); cf. Otto: Ann., **93**, 372 (1855).

CHAPTER XIV

THE HYDROUS OXIDES OF THE PLATINUM FAMILY

Each member of the two groups of three closely related metals which constitute the platinum family: ruthenium, rhodium, and palladium; and osmium, iridium, and platinum, forms two or more oxides. Some of these such as RuO_4 and OsO_4 can be obtained only in the anhydrous state, whereas others may be precipitated as flocculent or gelatinous masses containing varying proportions of adsorbed water.

THE HYDROUS OXIDES OF RUTHENIUM

Ruthenium Monoxide. Hydrous RuO is thrown down by alkali from the blue solution of $RuCl_2$. The precipitate is very highly dispersed, and the adsorbed alkali cannot be washed out without peptization taking place. The gel oxidizes very rapidly in the air. According to Remy,[1] the product of this spontaneous oxidation is hydrous Ru_2O_5; but the identity of the latter has not been established with certainty. Debray and Joly[2] prepared what they took to be $Ru_2O_5 \cdot 2H_2O$ by neutralizing an alkali ruthenate with nitric acid; but Gutbier and Ransohoff[3] showed the alleged compound to be a mixture of hydrous Ru_2O_3 with some higher oxide.

Ruthenium Sesquioxide. Hydrous Ru_2O_3 is precipitated by adding alkali to a solution of the corresponding chlorides.[4] Prepared in this way, the oxide contains adsorbed alkali that cannot be removed by prolonged washing.[5] Krauss and Kükenthal[6] obtained a chloride- and alkali-free product by evaporating the hydrochloric acid solution of $RuCl_3$ to dryness, redissolving in water, and adding just enough

[1] Z. anorg. Chem., **126**, 185 (1923).
[2] Compt. rend., **106**, 328, 1494 (1888).
[3] Z. anorg. Chem., **45**, 243 (1905); Gutbier: **95**, 177 (1916).
[4] Claus: Ann., **59**, 234 (1846); Joly: Compt. rend., **114**, 291 (1892); Brizard: Ann. chim. phys. (7) **21**, 311 (1900); Gutbier and Ransohoff: Z. anorg. Chem., **45**, 253 (1905).
[5] Gutbier: Z. anorg. Chem., **95**, 185 (1916); **109**, 206 (1920).
[6] Z. anorg. Chem., **132**, 315 (1924).

potassium hydroxide to the dark brown solution to cause complete precipitation of the oxide while the colorless liquid was still acid. The black flocculent precipitate analyzed for trihydrate or hydroxide, after washing thoroughly and drying in an atmosphere of nitrogen at 120°. These observations alone are insufficient to establish the existence of a trihydrate. Since the pure preparation is soluble in acids it furnishes a good starting point for making the most common ruthenium salts.

Ruthenium Dioxide. Hydrous RuO_2 is obtained by reduction of a solution of RuO_4 with 4% H_2O_2.[7] It settles out as a black flocculent precipitate which gives no clearly defined x-ray diffraction pattern. The precipitate[8] formed by evaporating a solution of $Ru(SO_4)_2$ with caustic potash is dark red in color and adsorbs alkali strongly. According to Gutbier,[9] the hydrous oxide cannot be obtained pure since it goes into colloidal solution very readily on washing.

THE HYDROUS OXIDES OF RHODIUM

Rhodium Sesquioxide. Hydrous Rh_2O_3 is precipitated as a black gelatinous mass by adding excess potassium hydroxide and a little alcohol to a solution of Na_3RhCl_6. If an excess of potash is not used, a sol is formed which deposits thin citron-yellow particles said to be $Rh(OH)_3 \cdot H_2O$.[10] The gelatinous oxide is readily soluble in acids, giving the corresponding rhodium salts.

Rhodium Dioxide. Hydrous RhO_2 separates as a green powder when chlorine is passed into a solution of Rh_2O_3 in alkali. If the flow of chlorine is continued, the green precipitate dissolves, giving a deep blue solution resembling the ammoniacal copper solution. The blue color is attributed to the alkali salt of rhodous acid, H_2RhO_3,[11] which decomposes gradually, precipitating hydrous RhO_2. If one attempts to dehydrate the hydrous dioxide, the anhydrous sesquioxide is obtained.[12]

THE HYDROUS OXIDES OF PALLADIUM

Palladium Monoxide. The addition of sodium carbonate to a solution of palladous salt precipitates hydrous PdO as a dark brown

[7] Krauss and Schrader: Z. anorg. Chem., **176**, 385 (1928).

[8] Claus: Ann., **59**, 234 (1846).

[9] Gutbier and Ransohoff: Z. anorg. Chem., **45**, 243 (1905).

[10] Claus: J. prakt. Chem., **76**, 24 (1859); **80**, 282 (1860); **85**, 129 (1862).

[11] Alvarez: Compt. rend., **140**, 1341 (1905).

[12] Wöhler and Ewald: Z. anorg. Chem., **201**, 145 (1931).

mass.[13]   When thrown down in the cold the oxide is readily soluble in alkalis, but it loses this property when dried or when precipitated from boiling solution, owing to coalescence of the particles.   The hydrous oxide is best obtained pure by hydrolysis of palladous nitrate. A PdO sol in paraffin oil has been introduced as a therapeutic agent under the name "Leptynol."[14]

Palladium Sesquioxide.   Hydrous Pd_2O_3 is best prepared by the electrolytic oxidation of a concentrated solution of palladous nitrate at 8° with a current density of 0.5 amp./cm^2; if the electrolysis is prolonged, hydrous PdO_2 is formed.   This is not a direct oxidation, but the sesquioxide decomposes into dioxide and monoxide, the latter dissolving in the free acid and undergoing further oxidation.[15]   The sesquioxide is formed also by the action of ozone on palladous nitrate. It is chocolate brown in color when first prepared, but on washing it gets darker owing to agglomeration of the particles and loss of adsorbed water.

Palladium Dioxide.   An impure hydrous PdO_2 is precipitated on adding caustic soda to a solution of K_2PdCl_6.   As mentioned above, it is obtained free from alkali and basic salt by the anodic oxidation of the nitrate, but it is not quite free from hydrous PdO.   The fresh oxide is soluble in acids, but like the monoxide, its reactivity decreases rapidly on standing.   It cannot be dehydrated[16] since it decomposes at ordinary temperatures under an oxygen pressure of 80 atmospheres.   It is, therefore, a vigorous oxidizing agent.

THE HYDROUS OXIDES OF OSMIUM

Osmium Monoxide and Sesquioxide.   Claus [17] prepared hydrous OsO by the action of warm concentrated alkali on $OsSO_3$ in an atmosphere of nitrogen.   It is a blue-black precipitate which takes up oxygen very rapidly from the air.   The same author obtained hydrous Os_2O_3 as a brown-red precipitate on adding alkali to a solution of K_3OsCl_6.

Osmium Dioxide.   A highly hydrous form of OsO_2 is precipitated by the addition of alkali to K_2OsCl_6, and by the action of alcohol

[13] Wöhler and König: Z. anorg. Chem., **46**, 323 (1905).

[14] Thorpe: "Dictionary of Chemistry," **5**, 51 (1924).

[15] Wöhler and Martin: Z. anorg. Chem., **57**, 398 (1908).

[16] Wöhler and König: Z. anorg. Chem., **46**, 323 (1905); **48**, 203 (1906); Wöhler and Martin: **57**, 398 (1908); Bellucci: Gazz. chim. ital., **35** I, 343 (1905); Z. anorg. Chem., **47**, 287 (1905).

[17] J. prakt. Chem., **90**, 65 (1863).

or other reducing agent on an alkali osmate such as K_2OsO_4.[18]   The hydrous mass may be converted into a fine powder by prolonged heating on the water bath in contact with the mother liquor.   If the gel is dried, it forms a horny body which loses water explosively and emits flashes of light when heated above 100°.   The more granular oxide, aged on the water bath, becomes incandescent quietly at the glow temperature.   It is obvious that the primary particles of the gel are extremely small, the coalescence on ignition causing a marked decrease in surface energy with the accompanying glow.   The gel is a typical hydrous oxide, the water content of which is determined by the conditions of drying.   The compound formed by hydrolysis of K_2OsO_4 in the presence of alcohol and hydrogen and by the action of sulfuric acid on K_2OsO_4 is hydrous OsO_2 and not H_2OsO_4, as claimed by Moraht and Wischin.[19]

Since the gel formed by reduction of alkali osmates contains such small primary particles, it can be peptized by shaking with an excess of water[17] or by treating with a small amount of alkali or ammonia.[20] Freundlich and Baerwind[21] dissolved 1 g of OsO_4 in 50 cc of water, added 10 cc of ethyl alcohol, and allowed the mixture to stand 24 hours.   The precipitate of the dark dioxide was washed with alcohol and peptized by shaking for several days with 800 cc of water.   The deep blue-black sol is fairly stable, but its stability is greater in the presence of a little alcohol or protecting colloid.[22]   The particles are negatively charged and are not spherical, as they appear alternately bright and dark when viewed with a cardioid ultramicroscope.

THE HYDROUS OXIDES OF IRIDIUM

Iridium Sesquioxide.   Hydrous Ir_2O_3 is obtained in much the same way as the corresponding rhodium compound, which it resembles closely.   When a solution of $IrCl_3 \cdot 6NaCl \cdot 24H_2O$ is heated with alkali in a stream of CO_2, an impure hydrous Ir_2O_3 separates that is greenish white to black in color, depending on the alkali concentration.   The light-colored product comes down from dilute alkali, whereas excess alkali gives the black oxide containing relatively

[18] Ruff and Borremann: Z. anorg. Chem., **65**, 429 (1910); Ruff and Rathsburg: Ber., **50**, 484 (1917).

[19] Z. anorg. Chem., **3**, 153 (1893).

[20] Ruff and Rathsburg: Ber., **50**, 484 (1917).

[21] Kolloid-Z., **33**, 275 (1923); cf. Szegvari: Z. physik. Chem., **112**, 277 (1924).

[22] Castoro: Z. anorg. Chem., **41**, 126 (1904); Paal and Amberger: Ber., **40**, 1392 (1907); **49**, 557 (1916); Amberger: Kolloid-Z., **17**, 47 (1915).

little water. This recalls the behavior of cupric hydroxide which dehydrates and darkens very quickly in the presence of alkali. Wöhler and Witzmann[23] peptized the green oxide in dilute hydrochloric and sulfuric acids; concentrated acids dissolve it, giving reddish yellow salts.

Iridium Dioxide. Hydrous IrO_2 is prepared by adding alkali to a hot solution of Na_2IrCl_6, the sesquioxide first formed being oxidized to dioxide in a current of oxygen.[24] The fresh preparation is fairly soluble in acids and alkalis, but it loses this property on drying.[25] The oxide can be gotten almost pure by drying the hydrous mass at 400° in carbon dioxide followed by boiling with alkali and subsequently with sulfuric acid.[23] The precipitate thrown down from a solution of $IrCl_4$ with KOH is said to have the composition $IrO_2 \cdot 2H_2O$ after washing with alcohol and drying in a vacuum desiccator.[26]

The color of the oxide varies from light blue through dark blue to black, depending on the size of the particles and the structure and water content of the mass. Like the sesquioxide the precipitate is darker and less hydrous when it comes down from strong alkali solution.

The solution obtained by the action of alkali on Na_2IrCl_6 in the cold has a violet color and contains hydrous IrO_2 in suspension; after a time, a violet modification of the oxide separates, which becomes blue on drying. Boiling the violet sol changes it to blue, probably owing to coalescence of the positively charged particles.[23] Dilute hydrochloric acid peptizes the desiccator-dried preparation, giving a blue sol.[27]

THE HYDROUS OXIDES OF PLATINUM

Platinum Monoxide. The black precipitate of hydrous PtO thrown down from $PtCl_2$ solution with caustic alkali cannot be washed free from chloride or alkali.[28] It is prepared in the pure state by adding the calculated amount of dilute caustic soda to a solution of K_2PtCl_4.[29] Since the fresh oxide takes up oxygen readily

[23] Z. anorg. Chem., **57**, 323 (1908).

[24] Claus: J. prakt. Chem., **39**, 104 (1846).

[25] Joly and Leidie: Compt. rend., **120**, 1341 (1895).

[26] Krauss and Gerlach: Z. anorg. Chem., **143**, 125 (1925).

[27] *Cf., also*, Paal: Ber., **50**, 722 (1917).

[28] Liebig: Pogg. Ann., **17**, 108 (1829).

[29] Thomsen: J. prakt. Chem. (2) **15**, 299 (1877); Wöhler: Z. anorg. Chem., **40**, 456 (1904); Wöhler and Frey: Z. Elektrochem., **15**, 133 (1909).

from the air, the precipitation, washing, and drying must be carried out in an atmosphere of carbon dioxide. When newly formed, it is readily soluble in dilute halogen acids but is insoluble in bases and in oxy-acids other than sulfurous. If it is dried in a vacuum desiccator, the water content corresponds approximately to the formula $PtO \cdot 2H_2O$, but this is probably not a definite hydrate. It holds on to its water very strongly, one sample retaining 6.6% water after heating several days at 400°.

Platinum Sesquioxide. Wöhler and Martin[30] obtained hydrous Pt_2O_3 for the first time in a pure condition by adding solid $PtCl_3$ to a solution of sodium carbonate. It is also formed by dissolving the chloride in concentrated potassium hydroxide and precipitating with acetic acid, but the latter product contains some PtO_2. The precipitate obtained at room temperature is light brown in color and highly hydrous; by boiling with alkali, it becomes less hydrous and darker; the dried preparation is almost black. The freshly formed oxide is not oxidized by boiling with water through which a stream of oxygen is passed; it cannot be dehydrated completely without decomposition.

Platinum Dioxide. Wohler[31] prepared pure hydrous PtO_2 by boiling a solution of H_2PtCl_6 with caustic potash, cooling, and neutralizing with acetic acid. The resulting precipitate is almost white, but becomes yellow on drying. Even when dried in the air the water content is less than corresponds to the tetrahydrate $PtO_2 \cdot 4H_2O$ or $H_2Pt(OH)_6$.[32] It loses water continuously by lowering the vapor pressure of the surroundings or by raising the temperature; the last 2.5% of water cannot be removed without decomposing the oxide. The freshly precipitated product is soluble in acids and alkalis, but the thoroughly dried substance is insoluble in all dilute and concentrated acids with the exception of hydrochloric and aqua regia. Although it forms no hydrates it is sometimes called platinic acid, since its reaction with alkalis yields platinates such as $K_2Pt(OH)_6$ isomorphous with the stannates.[33]

[30] Ber., **42**, 3958 (1909); *cf., however,* Dudley: Am. Chem. J., **28**, 59 (1902); Blondel: Ann. chim. phys. (8) **6**, 111 (1905).

[31] Z. anorg. Chem., **40**, 434 (1904); Topsöe: Ber., **3**, 462 (1870).

[32] Bellucci: Atti accad. Lincei (5) **12** II, 635 (1903).

[33] Bellucci and Parravano: Atti accad. Lincei (5) **14** I, 459 (1905).

CHAPTER XV

MORDANTS

The adsorption of many dyes by wool, silk, and cotton is so weak that they are of value to the practical dyer only when used in conjunction with mordants. The term mordant (from *mordre*, to bite or to corrode) was first applied by the French to metallic salts which were supposed to act by biting or opening a passage into the fibers of the cloth, giving access to the dye. Thus, alum was believed to be effective in fixing certain dyes, owing to the solvent or corrosive action of sulfuric acid.[1] It is now known that the real mordant is the hydrous oxide and not the acid derived from the salt.

In general, a mordant may be defined as any substance that is adsorbed strongly by the cloth and, in turn, adsorbs the dye strongly. In dyeing a mordanted cloth, it is the mordant rather than the fiber which adsorbs the dye in most cases. When a mordant adsorbs a dye in the absence of a fiber, the product is called a lake. The lakes employed as pigments are usually prepared in contact with what are termed lake bases, such as barium sulfate, china clay, red lead, and lead sulfate, which modify the physical properties of the lakes in some desired way.

In order to appreciate the importance of mordants in the art of dyeing, one needs but to recall that the first so-called direct or substantive dye, Congo red, was not discovered until 1884. Before this date it was impossible to dye cotton with acid and basic dyes except by the use of mordants. Moreover, substantive dyes on cotton are in general much less fast to light and washing than are the mordant colors.

A typical example of a mordant dye is alizarin, the important coloring matter of the roots of *Rubia tinctorium*, or madder, a plant of Indian origin which was cultivated largely in France and Holland before the synthesis of alizarin from anthracene was accomplished in 1868. If a piece of cotton is dipped into an aqueous solution of alizarin, it assumes a yellow color that is easily removed by washing

[1] Bancroft: "Philosophy of Permanent Colors," 1, 341 (1813); Napier: "A Manual of Dyeing," 186 (1875).

with soap and water; but if the cloth is first mordanted, it is dyed a fast color: red with alumina, reddish brown with chrome, orange with tin, and purple or black with iron. By treating the fiber with the so-called sulfonated oils before mordanting with alumina, there results the brilliant Turkey red, a color remarkable for its fastness to light and to the action of soap and water. The dyeing of Turkey red is a very ancient process having been carried out centuries ago in India, using milk as fatty matter and munjeet, the Indian madder plant. The plant itself with its earthy incrustations furnished enough alumina to give the color lake. The art spread from the East through Persia and Turkey, reaching France and England in the latter part of the eighteenth century.

Wool like cotton can be dyed with madder only by the aid of mordants. The scarlet trousers of the French soldiers, introduced by Louis Philippe to encourage madder culture, and the scarlet uniform of the British soldier of Revolutionary War days were made possible by the use of the mordant alumina.

Two classes of mordants are generally recognized: acid, and basic or metallic. The acid mordants are the tannins, the fatty acids, albumin, hydrous silica, arsenic acid, and phosphoric acid; the basic mordants are the hydrous oxides of the heavy metals.

The most important metallic mordants are the hydrous oxides of chromium, aluminum, iron, tin, and copper, in the order named. Alumina was the first mordant used, and years ago, alumina and stannic oxide were the most important because people were interested in getting the bright colors which these mordants yield. As might be expected, the mordanting action of nearly all the possible oxides has been investigated. Liebermann[2] reports that the oxides of yttrium, beryllium, thorium, cerium, zirconium, and copper hold dyes most tenaciously; the oxides of zinc, cadmium, manganese, antimony, bismuth, lead, tin, and thallium are much less satisfactory; and the oxides of iron, aluminum, chromium, and uranium occupy an intermediate position. Such a classification is not generally applicable; thus Wengraf[3] finds zirconia to be a stronger mordant for certain dyes than alumina, and the reverse is true in other cases. In any event, oxides of metals other than aluminum, chromium, iron, and tin are used only in special applications. For example, titania is reported to be a particularly good mordant to use with leather.[4] The principles involved

[2] Ber., **35**, 1493 (1902).
[3] Färber-Ztg., **25**, 277 (1914).
[4] Barnes: J. Soc. Dyers Colourists, **35**, 59 (1919).

in the mordanting process will be illustrated in a brief discussion of the nature and applicability of the more important mordants.

ALUMINA

Aluminum salts in aqueous solution hydrolyze in accord with the following equation: $AlA_3 + xH_2O \rightleftarrows Al_2O_3 \cdot xH_2O + 6HA$, in which A represents the anion. This reaction proceeds further to the right, the more dilute the solution, the weaker the acid formed, and the higher the temperature. As we have seen, it is difficult to prepare a sol in the presence of sulfate because of the precipitating power of the divalent anion. The amount of hydrous oxide formed in a given case is increased by removal of hydrogen ion with alkali; but the range of hydrogen ion concentration in which the oxide precipitates is much wider with salts of strongly adsorbed multivalent ions, such as sulfate, than with salts of univalent ions.

Although aluminum may form basic salts under certain conditions, it is certain that the vast majority of the alleged basic acetates described by Crum,[5] and of the basic nitrates, chlorides, sulfates, acetates, and sulfoacetates formulated by Liechti and Suida,[6] are wholly without experimental foundation. By adding alkali to aluminum sulfate, a phase separates below $pH = 5.5$ having approximately the composition $5Al_2O_3 \cdot 3SO_3$;[7] but the ease with which the sulfate can be displaced from the precipitate by a variety of inorganic and dye cations argues against its being a definite basic salt.

Since aluminum salts hydrolyze of themselves, one would expect the hydrolysis in a given case to proceed further in the presence of a fiber which adsorbs hydrous alumina. This is actually so, as will be shown in the following paragraphs.

Mordanting of Wool

Aluminum Sulfate. When wool is treated with solutions of aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$, less than 5% on the wool, the bath is exhausted completely, all the alumina and the sulfuric acid being adsorbed.[8] At higher salt concentrations, more and more remains in the bath. Knecht[9] believes that both hydrous oxides and

[5] Ann., **89**, 168 (1854).

[6] J. Soc. Chem. Ind., **2**, 537 (1883); cf., also, Schlumberger: Bull. soc. chim. (3) **13**, 41 (1895); Böttinger: Ann., **244**, 224 (1888).

[7] Miller: U. S. Pub. Health Repts., **38**, 1995 (1923); Williamson: J. Phys. Chem., **27**, 284 (1923).

[8] Liechti and Schwitzer: Mitt. techn. Gewerbe-Museums in Wien, Sektion für Färberei, **3**, 47 (1886).

[9] Knecht, Rawson, and Löwenthal: "A Manual of Dyeing," 237 (1916).

true basic aluminum salts are deposited by the mordanting process, since the spent liquors on dyeing well-washed wool with alizarin always possess an acid reaction. This evidence of basic salt formation is inconclusive, since adsorbed sulfuric acid would be displaced quite as readily as acid in definite chemical combination. Fürstenhagen and Appleyard[10] give data to show that the amount of sulfate taken up by wool remains constant when the fiber is mordanted from potash alum solutions containing 10–20% of alum referred to the wool. According to Havrez[11] and to von Georgievics,[12] the amount of alumina taken up by wool from relatively dilute potash alum solutions
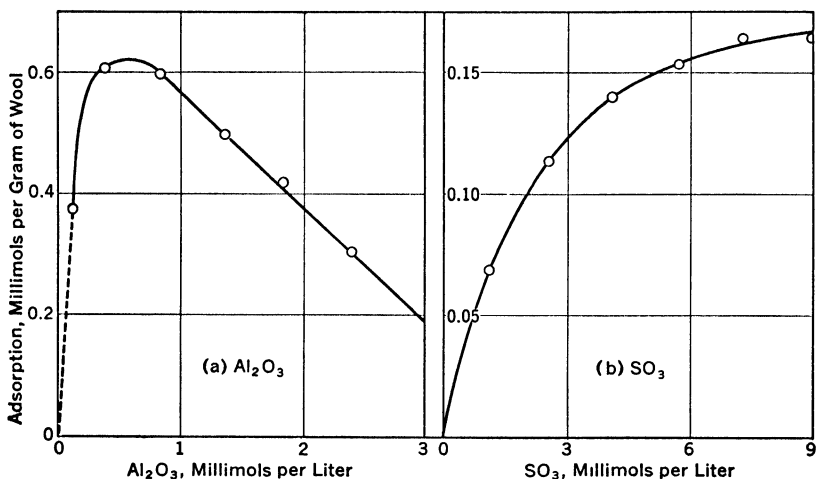
FIG. 57.—Adsorption of Al_2O_3 and SO_3 by wool.

is greater than the amount of sulfuric acid; but with increasing salt concentration, the amount of sulfuric acid taken up increases relatively to the alumina until, at 24% alum referred to the wool, the alumina and acid are taken up in the same relative amounts as they occur in aluminum sulfate.[13] Some observations of Paddon[14] are of importance in this connection. Two-gram samples of well-washed wool were boiled for 1 hour in potash alum solution of varying strengths, after which the wool was removed and aliquot portions of the several baths

[10] J. Soc. Dyers Colourists, 105 (1888).
[11] Chem. Zentr., 696 (1872).
[12] J. Soc. Chem. Ind., 14, 653 (1895).
[13] Cf. Thenard and Roard: Ann. chim. phys., 74, 267 (1810).
[14] J. Phys. Chem., 26, 790 (1922).

were analyzed in the usual gravimetric manner for both aluminum and sulfate. The resulting data are shown graphically in Fig. 57a and b. Both curves are smooth and free from sudden breaks, indicating that the mordanting of wool with potash alum does not lead to the formation of definite compounds on the fiber, but that the process is an adsorption phenomenon involving both alumina and sulfuric acid. It is probable that the acid is adsorbed both by the alumina and by the wool.

The adsorption curve for alumina passes through a maximum due to precipitation of considerable oxide on boiling the solutions of higher concentration, thereby cutting down the concentration of alumina so far as the wool is concerned. The adsorption of SO_3 follows a continuous course, approximating saturation when the concentration is in the neighborhood of 7 millimols per liter. Above this concentration the adsorption is necessarily almost constant; hence this should not be construed as indicating the adsorption of a definite basic salt on the fiber.

The purpose of the mordant is to have something on the fiber which will adsorb and hold the coloring matter. It is important, therefore, to have the mordant taken up under such conditions that it will be held most tenaciously by the cloth, have the maximum transparency, and adsorb the greatest amount of dye. As Bancroft[15] points out, one would not ordinarily expect to obtain the mordant in such a form that it will satisfy all these requirements to the maximum degree, simultaneously, but the aim should be to get the mordant in the form which is most generally useful. One objection to alum or aluminum sulfate for mordanting wool is that sulfate ion coagulates alumina too readily, thereby precipitating perceptible amounts of the hydrous oxide in the bath or superficially on the wool in a form that does not hold well. This is particularly true with more concentrated baths, as noted by Havrez[16] and Paddon.[17] The former recommends a bath containing less than 10% alum referred to the amount of wool, otherwise the mordant washes off readily and the wool is not dyed deeply when treated with the coloring matter. As one would expect, the so-called basic solutions of aluminum sulfate cannot be used at all with wool, since the precipitation of the hydrous oxide is altogether too rapid. Liechti and Schwitzer[18] claim that alum does not give as good a mor-

[15] J. Phys. Chem., **18**, 399 (1914).
[16] Dinglers polytech. J., **205**, 491 (1872).
[17] J. Phys. Chem., **26**, 791 (1922).
[18] J. Soc. Chem. Ind., **5**, 526 (1886).

dant as aluminum sulfate. This may be due to one or more of the following causes: the increase in the hydrolysis of aluminum sulfate by the presence of sodium sulfate;[19] the detrimental precipitating action of the excess sulfate in alum; and the increasing of the relative amount of sulfate adsorbed. Addition of sulfuric acid to alum causes the mordant to penetrate more thoroughly and to be fixed better than when the normal sulfate is used.[20] This is because the cutting down of the hydrolysis by the increased acidity is more pronounced than the agglomerating action of the increased concentration of sulfate.

Aluminum Salts of Organic Acids. The rapid precipitation of hydrous oxide in a loose condition on the surface of the cloth may be obviated by using an aluminum salt of a weaker acid such as aluminum tartrate, lactate, or oxalate. Although the organic salts hydrolyze more readily than the sulfate, the resulting hydrous oxide is held in a more highly peptized state. Accordingly, the mordanting is deeper and more uniform from solutions of these salts or from a solution of aluminum sulfate to which is added a so-called mordanting assistant such as cream of tartar, tartaric acid, or oxalic acid. Some observations of Miller[21] are of interest in this connection: Portions of a solution $0.005\ M$ with respect to $AlCl_3$ and $0.0075\ M$ with respect to $K_2C_2O_4$ were treated with gradually increasing amounts of alkali. A slightly opalescent sol but no precipitate was formed until the pH value of the solution reached 8.8. In striking contrast to this, a $0.0025\ M$ solution of potash alum formed a precipitate at as low a pH value as 4.3 and up to 8.9. Obviously the tendency of hydrous alumina to agglomerate under the above conditions is much less in the presence of oxalate than of sulfate. It is probable that the behavior of tartrate is similar to that of oxalate, since the mordant obtained in the presence of the former is even more satisfactory than that formed in the presence of the latter.

The beneficial influence of organic acids on the mordanting process has received widely diversified interpretations from time to time. Thus, Knecht, Rawson, and Löwenthal[22] claim that the aluminum salts of tartaric and oxalic acids possess a certain resistance to the dissociating action of wool; this is, of course, inaccurate, since the salts of the weaker acids hydrolyze more readily than sulfate. Beech[23]

[19] Liechti and Suida: J. Soc. Chem. Ind., **2**, 537 (1883).

[20] Liechti and Schwitzer: J. Soc. Dyers Colourists, 161 (1886).

[21] U. S. Pub. Health Repts., **40**, 351 (1925).

[22] "A Manual of Dyeing," 236 (1910).

[23] "The Principles and Practice of Wool Dyeing," 71 (1902).

says that the addition of a little oxalic acid, cream of tartar, or tartaric acid to the mordanting bath helps in the decomposition of the metallic salt by the wool fiber; but this seems improbable, as the addition of an acid cuts down the hydrolysis. Herzfeld[24] offers no explanation of the phenomenon, but he recognizes clearly that the loose and uneven character of the mordant obtained with aluminum sulfate alone is due to the rapidity with which the salt decomposes; and that the presence of cream of tartar, oxalic acid, or lactic acid causes the precipitation to take place more slowly and regularly, thereby giving a more satisfactory mordant.

Mordanting of Silk

Silk adsorbs hydrous alumina somewhat less strongly than wool and must, therefore, be mordanted from slightly more basic solutions. The solutions employed are aluminum sulfate,[25] alum,[26] and sulfate-acetate and nitrate-acetate mixtures. Heermann[27] made observations which leave little room to doubt but that the real mordants are the hydrous oxides, at least with silk. In these experiments, both raw and boiled-off[28] silk were treated with various mordanting baths at 30°, and the mordanting fiber was analyzed for both metallic oxide and acid radical. The results have been collected in Table XXII.

TABLE XXII

Mordanting solution	Nature of silk	Ratio of adsorbed oxide to adsorbed acid radical
Stannic chloride...............................	Raw	$155SnO_2 : 1Cl$
Stannic chloride...............................	Boiled off	$143SnO_2 : 1Cl$
Ferric sulfate (basic).........................	Raw	$111Fe_2O_3 : 1SO_3$
Ferric sulfate (basic).........................	Boiled off	$91Fe_2O_3 : 1SO_3$
Chromic chloride..............................	Raw	$40Cr_2O_3 : 1Cl$
Chromic chloride..............................	Boiled off	$44Cr_2O_3 : 1Cl$
Aluminum acetate............................	Raw	Al_2O_3 only, adsorbed
Aluminum acetate............................	Boiled off	Al_2O_3 only, adsorbed

[24] "Das Färben und Bleichen der Textilfasern," 58 (1900).
[25] Ganswindt: "Theorie und Praxis der modernen Färberei," 2, 18 (1903).
[26] Knecht, Rawson, and Löwenthal: "A Manual of Dyeing," 238 (1916).
[27] J. Soc. Chem. Ind., 23, 1143 (1904).
[28] Immersed in a good neutral Marseilles or olein soap solution at 90–95°, in order to remove the silk gum or pericine from the fibers.

Heermann looks upon mordanting as a catalytic process in which the fiber decomposes the mordanting salts catalytically, giving hydrous oxides that become fixed on the fiber and acids that remain in the bath. Although the hydrolysis of the mordanting salts is increased, owing to strong adsorption of the hydrous oxides by the fiber, the process is not catalytic, since a given amount of fiber can increase the decomposition of only a limited amount of salt, and the mordanted fiber is not in the same condition after the process as before.

The mordanting of silk may be carried out satisfactorily at 15–20°. At as low a temperature as 0–5° the mordanting salts do not penetrate the fiber well and the adsorption of the hydrous oxides takes place slowly and irregularly.[29]

Mordanting of Cotton

It has been recognized for a long time that normal aluminum sulfate and alum cannot be used as mordants for cotton.[30] This is because the cotton adsorbs hydrous alumina much less strongly than wool or silk and so does not decompose solutions which are distinctly acid. If the acidity of the alum solutions is reduced by the addition of sodium carbonate, they can be used to mordant cotton. Liechti and Suida[31] showed that the amount of alumina fixed is greater the more basic the mordanting solutions. Since cotton adsorbs hydrous alumina less strongly than wool, the mordant is fixed less strongly by cotton than by wool;[32] accordingly, we should expect the relatively large amounts of mordant taken up from highly basic solutions to rub off readily. Tingle[33] claims that hydrous alumina is adsorbed neither from aluminum sulfate nor basic aluminum sulfate solutions. His results with aluminum sulfate confirm those of everybody else, but the observations with basic aluminum sulfate cannot be generally true, since such solutions have been used in mordanting cotton without a fixing agent.[34]

Aluminum acetate appears to be the best mordanting bath for cotton. This is because the salt hydrolyzes readily and gives the hydrous oxide in the form of a highly dispersed sol which can penetrate

[29] Heermann: J. Soc. Chem. Ind., **22**, 623 (1903); **23**, 57 (1904).

[30] Cf. Bancroft: "Philosophy of Permanent Colors," **1**, 357; **2**, 148, 242 (1813).

[31] J. Soc. Chem. Ind., **2**, 538 (1883); cf. Keitschera and Utz: Mitt. techn. Gewerbe-Museums in Wien, Sektion für Färberei, **3**, 110 (1886).

[32] Bancroft: J. Phys. Chem., **26**, 501 (1922).

[33] Ind. Eng. Chem., **14**, 198 (1922).

[34] Knecht, Rawson, and Löwenthal: "A Manual of Dyeing," 233 (1916).

into the fiber and be adsorbed. The use of aluminum formate[35] and aluminum lactate[36] in place of the acetate has been suggested; but the principle is the same with all salts of weak organic acids. Cotton is not mordanted from a solution of "sodium aluminate," but the latter is used to pad on hydrous alumina in calico printing.[37] This is accomplished by precipitating hydrous alumina on the cloth by adding ammonium chloride to the aluminate bath. Fixing agents (p. 356) are sometimes used in mordanting cotton with alumina.

Mercerized cotton adsorbs substantive dyes[38] and takes up basic mordants[39] more strongly than does ordinary cotton. This is not because the mercerized fiber is a definite chemical compound between cotton and sodium hydroxide[40] as some[41] believe, but is probably due to the retention of alkali in the channels of the cotton fibers or to a change in the structure of the cotton as a result of the mercerization process.

CHROME

Mordanting of Wool

Sodium Bichromate. Chrome is by far the most important mordant used with wool. The mordanting bath most commonly used is an acid solution of bichromate instead of the metallic salt as in the case of alumina. Before the war, the readily crystallized potassium bichromate was employed, but the demand for a cheaper product led to the development of a pure crystalline form of sodium bichromate which has displaced the potassium salt for mordanting purposes.[42]

From the bichromate solution, wool adsorbs chromic acid which is subsequently reduced to chromic oxide, the real mordant. Chromic acid is not held very strongly[43] by the fiber, and practically all of it can be removed by washing.[44] Wool itself has been shown to reduce chromic acid,[43] but this involves more or less waste,[45] so that a reducing agent is usually added either by itself or in the form

[35] Schwalbe: Kolloid-Z., **5**, 129 (1909).

[36] Boehringer and Sons: Z. Farben-Ind., **9**, 237, 253 (1910).

[37] Ganswindt: "Theorie und Praxis der modernen Färberei," **2**, 212 (1903).

[38] Matthews: "Application of Dyestuffs," 165, 278 (1920).

[39] Schaposchnikov and Minajew: Z. Farben-Ind., **3**, 165 (1904); **4**, 81 (1905).

[40] Leighton: J. Phys. Chem., **20**, 188 (1916); Bancroft and Calkin: **39**, 1 (1935).

[41] Cf. Ganswindt: "Theorie und Praxis der modernen Färberei," **2**, 215 (1903).

[42] Matthews: "Application of Dyestuffs," 344 (1920).

[43] Liechti and Hummel: J. Soc. Chem. Ind., **12**, 244 (1893).

[44] Bancroft: J. Phys. Chem., **26**, 737 (1922); cf., *however*, Whiteley: J. Soc. Chem. Ind., **6**, 131 (1887).

[45] Durfee: Am. Dyestuff Rep., **9**, No. 10, Tech. Sec. 20–23 (1921).

of a dye, such as logwood[46] or alizarin;[43] under these conditions, the wool is not attacked appreciably. Chromic acid mordants wool more strongly than either neutral chromate or bichromate,[46] so that, in practice, a suitable amount of acid is added to the bichromate bath. Within limits, increasing the acid concentration increases the amount of chromic acid adsorbed.[47] This is less marked with sulfuric acid than with either hydrochloric or nitric acid, probably because sulfuric acid is more strongly adsorbed by wool than hydrochloric or nitric acid and so is more effective in cutting down the adsorption of chromic acid.[48] The importance of sulfate ion is further indicated by the fact that a mixture of sodium chloride and sulfuric acid behaves like sulfuric acid and not like hydrochloric. The presence of sulfuric acid is more effective than an equivalent amount of either hydrochloric or nitric acid in causing the oxidation of wool by chromic acid. Since the oxidizing power of chromic acid is greater the higher the concentration of acid, and since sulfuric acid is adsorbed by wool more strongly than hydrochloric or nitric acid, Bancroft[49] attributes the greater effect of sulfuric acid to higher acid concentration at the surface of the wool.

A bichromate bath acidified with sulfuric acid is objectionable, not only because the reduction of chromic acid takes place at the expense of the wool, but also because some chromic oxide remains in the mordant and oxidizes such colors as alizarin blue, alizarin yellow, etc., producing weak shades that may be undesirable.[50] As a matter of fact, the customary thing is to use an organic acid or acid salt such as cream of tartar, tartaric acid, oxalic acid, formic acid,[51] or lactic acid.[52] Since these so-called assistants are oxidized by chromic acid, it is probable that little or no oxidation of the wool takes place in their presence. Moreover, they bring about a uniform deposit of the mordant in a form highly satisfactory for receiving the dye.[53]

Chromic Salts. Since wool adsorbs chrome from chromic salt

    [46] Matthews: "Application of Dyestuffs," 477 (1920).

    [47] Hummel and Gardner: J. Soc. Chem. Ind., 14, 452 (1895).

    [48] Bancroft: J. Phys. Chem., 26, 743 (1922).

    [49] J. Phys. Chem., 26, 744 (1922).

    [50] Beech: "The Principles and Practice of Wool Dyeing," 116 (1902).

    [51] Kapff: Z. Farben-Ind., 4, 159 (1905); Whittaker: "Dyeing with Coal Tar Dyestuffs," 50 (1919).

    [52] Knecht, Rawson, and Löwenthal: "A Manual of Dyeing," 173, 256 (1916).

    [53] Knecht, Rawson, and Löwenthal: "A Manual of Dyeing," 256 (1916); Beech: "The Principles and Practice of Wool Dyeing," 117 (1902).

solutions, the latter may be used for mordanting baths under suitable conditions. It is claimed that chrome alum alone does not give a satisfactory bath because the mordant is not adsorbed evenly and the subsequent dyeing is not uniform. Since aluminum alum gives a good mordant, it would appear that the difficulty with chrome alum could be corrected by a suitable adjustment of the temperature, concentration, or basicity of the bath. The addition of cream of tartar, oxalic acid, or tartaric acid to the chrome alum bath gives a satisfactory mordant, as does chromium oxalate[54] or chromium tartrate, but not chromium acetate or chromium fluoride.[55]

Liechti and Hummel[56] observed increased mordanting with increasing concentration of chrome alum, just as would be expected. They also claimed to get an increased amount of chromium taken up by increasing the sulfuric acid content of the alum bath; but this is improbable, if not impossible, unless the heating is conducted in such a manner that a precipitate forms in the bath and is padded on the fibers. The reported increase in adsorption with increasing sulfuric acid content is contradicted by the further observation of Liechti and Hummel that the bath is exhausted less completely the greater the concentration of sulfuric acid.

It is probable that the mordant is chromic oxide with more or less adsorbed sulfate rather than a basic chromic sulfate as assumed by Liechti and Hummel. However, at least one definite crystalline basic sulfate, $[Cr(OH)_2(H_2O)_4]_2SO_4$, has been prepared;[57] so the formation of a basic salt on the fiber must be regarded as a possibility.

Wool is mordanted very slightly from solutions of chromic chloride or nitrate,[58] probably because the degree of hydrolysis is low and the peptizing action of these solutions for hydrous chromic oxide is too great to yield the mordant to the fiber. If this be true, the addition of a suitable amount of soda to the chloride or nitrate solution should give a satisfactory mordanting bath.

Mordanting of Silk and Cotton

Silk adsorbs chromic oxide less strongly than wool; but it is possible to mordant it from a bath of chrome alum or chromic chloride

[54] Tagliani: Color Trade J., 11, 158 (1922); Textile Colorist, 44, 650 (1922).

[55] Liechti and Hummel: J. Soc. Chem. Ind., 13, 356 (1894).

[56] J. Soc. Chem. Ind., 13, 222, 356 (1894).

[57] Werner: Ber., 41, 3447 (1908); cf., also, Williamson: J. Phys. Chem., 27, 280 (1923).

[58] Liechti and Hummel: J. Soc. Chem. Ind., 13, 224 (1894).

but not of bichromate.[59]   To preserve the luster of silk, Whittaker[60] recommends mordanting it over night in a cold chromic chloride bath followed by treating with sodium silicate to fix the mordant on the fiber (p. 356).

The adsorption of chromic oxide by cotton is so weak that no mordanting whatsoever takes place from a 10% chrome alum bath. Apparently no completely satisfactory bath has been found for mordanting cotton, especially cotton yarns, with chrome.[61]   The best bath is the colloidal solution of hydrous chromic oxide in alkali, the so-called alkali chromate bath.[62]   This cannot be used for yarns on account of the caustic action on the hands of workmen; nor can it be used on oiled material since the oil would be stripped from the fiber.   A chromic acetate bath is fairly successful since the acetic acid may be removed by heating.

IRON

Mordanting of Wool

At one time, ferrous sulfate was widely used for mordanting wool; but it has been largely replaced by chrome mordant.   The iron mordant is still of importance in dyeing logwood blacks, since the latter on chrome mordant are likely to turn green on exposure to light.   Moreover, it is claimed that cloth mordanted with copperas possesses a "kinder" and softer handle than cloth mordanted with chrome.   In general, iron mordants tend to "sadden" or darken the shade of most dyes, and they are therefore used chiefly for dark colors, especially browns and blacks.

A copperas black may be obtained by mordanting either before or after dyeing.   The latter process, which is usually employed, consists essentially in boiling the wool in a decoction of dyewoods for a time and then adding copperas directly to the bath.   When the fiber is mordanted before dyeing, it is necessary to add comparatively large quantities of tartaric or oxalic acid to prevent unequal precipitation of the oxide of iron on the fiber.   Before placing the mordanted cloth in the dye bath, better results are obtained by allowing it to lie for several hours in the air, whereby hydrous ferrous hydroxide is oxidized more or less completely to the ferric state.   A probable reason for this is that hydrous ferric oxide is a better adsorbent than the more coarsely crystalline ferrous hydroxide.

[59] Knecht, Rawson, and Löwenthal: "A Manual of Dyeing," 258 (1916).
[60] "Dyeing with Coal Tar Dyestuffs," 50 (1919).
[61] Knecht, Rawson, and Löwenthal: "A Manual of Dyeing," 252 (1916).
[62] Koechlin: Dinglers polytech. J., 254, 132 (1884).

Mordanting of Silk

Iron salts are quite extensively used in mordanting silk for dyeing black, especially with logwood.   Alumina and tin mordants are of minor importance, and chrome is seldom used as a mordant for logwood; nor is logwood used to produce any color on silk other than black.   For the dyeing of silk, the mordants are applied in sufficient amount not only to take up the dye but also to add appreciably to the weight of the silk.   Raw silks adsorb the hydrous oxide fairly strongly; but it is customary to impregnate the fiber with tannin before putting it in the iron bath which is usually ferrous acetate. By repeated treatment in the tannin and salt baths, the weight of the silk fiber may be increased as much as 400%.   If a ferric salt such as basic ferric sulfate is employed, the fiber is first mordanted with the hydrous oxide which is subsequently "fixed" in a tannin bath.

Although raw silk adsorbs and holds the hydrous iron oxides fairly strongly, boiled-off silk possesses but a slight adsorption capacity for the mordant.   The boiled-off silk is therefore dipped in the iron liquor and subsequently put into a boiling soap solution containing olein soap and a little soda, which precipitate hydrous ferric oxide on the fiber in an aged condition.   This operation may be repeated several times according to the amount of weighting desired.

Mordanting of Cotton

Cotton shows a much weaker adsorption for hydrous ferric oxide than either wool or raw silk.   It is, therefore, mordanted by a process similar to that employed with boiled-off silk, namely, by saturating in a solution of basic ferric sulfate followed by treating with lime water or soda solution which precipitates the hydrous oxide in the cloth. If ferrous sulfate is employed, the fiber is first mordanted with tannin, which adsorbs the ferrous hydroxide strongly; and any sulfate adsorbed is subsequently removed by washing with lime water.   After mordanting, the adsorbed hydroxide is allowed to oxidize in the air before placing in the dye bath.

TIN

Mordanting of Wool and Cotton

Wool is seldom mordanted with tin mordant, but when this is done, the bath consists of stannous chloride in conjunction with oxalic or tartaric acid.   Considerably more acid is said to be taken up from stannic salt than from stannous salt baths, which accounts

for the use of the latter in practice. As in mordanting with alumina, the presence of an organic acid is necessary to prevent rapid, uneven deposition of the hydrous oxide on the fiber. Stannous tartrate or stannic tartrate alone are said to be unsatisfactory, but it is possible that the addition of an excess of either tartaric or oxalic acid would make a good mordanting bath if there were any point in avoiding the use of chloride.

Stannic salts may be used as a bath to mordant cotton, but the adsorption of the oxide is so weak that the fiber must first be mordanted with tannin. If a bath of sodium stannate is employed, the cloth is first impregnated with a solution of the salt and is then passed through a very dilute solution of sulfuric acid or aluminum sulfate. Hydrous stannic oxide, or, if an aluminum salt is used, a mixture of the hydrous oxides of tin and aluminum, is precipitated and constitutes the mordant.

Mordanting and Weighting of Silk

Silk treated with stannic chloride takes up 9–43% SnO_2, depending on the concentration. The various combinations give x-radiograms of only SnO_2 and silk, indicating the absence of any crystalline compound of tin and protein.[63]

The most important use of tin salts in the dyeing industry is in the mordanting and weighting of silk.[64] The cloth is first steeped in a solution of stannic chloride and, after rinsing, is put into a bath of sodium phosphate and subsequently into one of sodium silicate. The process must be repeated several times in order to give the silk the desired weight.[65]

If the silk is weighted excessively by the tin-phosphate-silicate process, serious faults may develop in the goods. Thus, heavily weighted silk frequently becomes quite tender when exposed even for a short time to direct sunlight.[66] Moreover, reddish-colored tender spots often appear in pieces, after storing. Gnehm, Roth, and Thomann[67] first attributed the formation of these tender spots to the action of perspiration, but this cannot be true, as unused goods frequently show the damaged spots. Sisley[68] pointed out that the only constituent of perspiration which has an injurious effect is the

[63] Elöd, Pieper, and Silva: Z. angew. Chem., **41**, 14 (1928).

[64] Heermann: J. Soc. Dyers Colourists (1903–1906); Neuhaus: Knecht, Rawson, and Löwenthal's "A Manual of Dyeing," 278 (1916).

[65] Gnehm and Baenziger: J. Soc. Dyers Colourists, 40 (1897).

[66] Knecht, Rawson, and Löwenthal: "A Manual of Dyeing," 279 (1916).

[67] J. Soc. Dyers Colourists, 256 (1902).

[68] J. Soc. Dyers Colourists, 276 (1902).

salt; and Meister[69] showed that the deterioration of the silk is due to active chlorine produced by the catalytic action of copper which is always present in small quantities as a result of careless handling during spinning and weaving. As a preventive, Meister[69] suggests padding the goods in a very weak solution of ammonium thiocyanate; but this is not infallible. The use of thiourea and its salts has been patented for the same purpose.[70]

Since silk adsorbs hydrous stannic oxide, leaving most of the hydrochloric acid, the bath becomes strongly acid by continued use. To keep it in good condition, stannic chloride must be replaced and the excess hydrochloric acid neutralized with ammonia from time to time. After the ammonium chloride content of the liquor becomes too high for satisfactory mordanting, a fresh bath must be employed.

TANNIN

Having considered the most important basic mordants, it seems advisable to point out the essential characteristics of a typical acid mordant. The class of substances known as the tannins, to which tannic acid belongs, is seldom employed in mordanting wool but finds its chief use in mordanting cotton and linen, in "fixing" the hydrous oxide mordants on cotton, and in weighting silk with hydrous ferric oxide (p. 353).
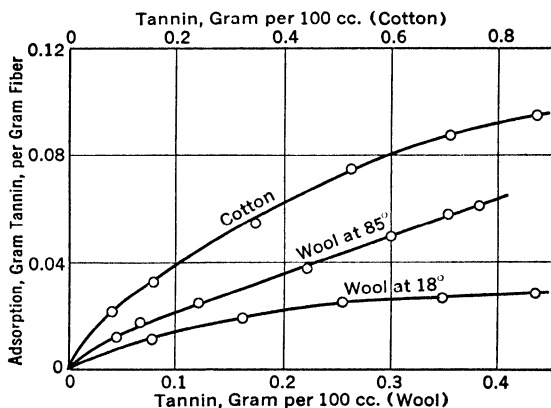
FIG. 58.—Adsorption of tannin by wool and cotton.

Both wool and cotton adsorb tannin from its colloidal solution in water, the amounts taken up varying continuously with the concentration of the sol, as shown by the curves in Fig. 58 constructed from the data of Pelet-Jolivet[71] on the adsorption by wool and of Sanin[72] on the adsorption by cotton.

[69] J. Soc. Dyers Colourists, 192 (1905).
[70] J. Soc. Dyers Colourists, 51 (1907).
[71] "Die Theorie des Färbeprozesses," 79 (1910).
[72] Kolloid-Z., 10, 82 (1912).

The adsorption of tannin by wool is not very marked, especially at ordinary temperatures, but it increases with the temperature; on the other hand, the adsorption by cotton apparently decreases with increasing temperature of the bath.[73] If mixed cotton goods containing wool are mordanted at ordinary temperature, the cotton only is mordanted to an appreciable extent.

Since tannin is an acid mordant, one might expect the adsorption to be reduced in alkaline solution and increased in acid solution. As a matter of fact, the adsorption of tannin is cut down almost to zero in the presence of alkali; and acetic acid increases the adsorption[74] which, however, passes through a maximum at high concentration.[75] Sulfuric acid, on the other hand, cuts down the adsorption, and hydrochloric acid has little effect. This behavior with different acids is probably due to the difference in the adsorption of the acids by cotton. We know, for example, that sulfuric acid is adsorbed by cotton more strongly than hydrochloric,[76] which would account for the adsorption of tannin being cut down more by the former than by the latter. Different salts added to the bath all seem to increase the adsorption of tannin, possibly because they decrease the stability of the sol.

Although tannin is adsorbed quite strongly by cotton, it must be "fixed" on the fiber before the dyeing process. The best fixing agents are antimony salts, but salts of tin, aluminum, and iron are used in special cases.

FIXING OF MORDANTS

In connection with the mordanting of cotton which does not hold the hydrous oxides firmly, mention has been made of the addition of fixing agents to bring about the desired results. This practice is followed whenever the single mordant is not adsorbed sufficiently strongly. For example, sodium phosphate may be used for fixing alumina and tin; sodium arsenate, soap, and tannin for iron; sodium silicate and tannin for chrome and tin; salts of antimony, tin, aluminum, and iron for tannin; etc. In other words, the acid mordants—tannin, fatty acid salts, arsenates, silicates, and phosphates—are used as fixing agents for the basic or metallic mordants; and the basic mordants are used as fixing agents for the acid mordants.

[73] Knecht and Kershaw: J. Soc. Dyers Colourists, 40 (1892); Ganswindt: "Theorie und Praxis der modernen Färberei," 2, 216 (1903).

[74] Knecht, Rawson, and Löwenthal: "A Manual of Dyeing," 188 (1916).

[75] Dreaper: "The Chemistry and Physics of Dyeing," 161 (1906).

[76] Leighton: J. Phys. Chem., 20, 188 (1916).

Mechanism of the Process

The question arises as to whether the fixing process consists, as generally assumed, in the formation of definite chemical compounds such as antimony tannate, iron arsenate, or tin phosphate, which are more strongly adsorbed by the fiber than the single mordants, or whether the fixed mordants are mixtures of indefinite composition. In the light of the evidence, the latter view is the more probable in the vast majority of cases.   To illustrate: it is known that precipitated hydrous ferric oxide is peptized as a positive sol on washing and that tannin is peptized by water as a negative sol.   If the two are brought in contact in suitable amounts, mutual adsorption takes place and each prevents the other from being peptized to the sol state; in other words, a mutual "fixing" results.   The so-called iron tannates are not definite compounds.

The case of the action between antimony salts and tannin has been studied by Sanin,[77] who believes there are at least three definite antimony tannates.   These cannot be obtained pure, but at first, Sanin preferred to regard different products as mixtures of two or more antimony tannates rather than as substances of continuously varying composition.   Later[78] he concluded that adsorption does occur when tannin and potassium antimony tartrate are mixed, but that tannates are formed during the technical procedure used in mordanting with tannin.   Although no one can question the possibility of forming a true antimony tannate under special conditions, it is altogether improbable that the varied conditions in technical practice are such as to yield a definite salt.

Wislicenus and Muth[79] found that the amount of tannin taken up by fibrous alumina increases rapidly at first with increasing concentration of the tannin sol and then attains an approximately constant value. This constant value is the limiting adsorption value for the particular alumina and does not indicate the formation of aluminum tannate. Had a different alumina been used, the saturation value would have been found at a different point.   Von Schröder[80] showed that the taking up of tannin, both from the solution in alcohol and from the aqueous sol, is an adsorption phenomenon and no aluminum tannates are formed.

It is a moot question whether the fixing of iron oxide or alumina

[77] Z. Farben-Ind., 9, 2, 17, 49 (1910).
[78] Sanin: Kolloid-Z., 13, 305 (1913).
[79] Kolloid-Z., 2, 2nd Supplement, XVIII (1908).
[80] Kolloid-Beihefte, 1, 1 (1909).

by oil mordants is an adsorption phenomenon or is due to the forma-
tion of salts of fatty acids. In this connection, Knecht, Rawson, and
Löwenthal[81] say: "The amount of iron which is taken up by the fiber
depends less on the strength of the mordanting liquor than on the
amount of oil that has already been fixed in the material; the oil
attracts the oxide of iron with great energy so that it is not readily
stripped from the fiber even by comparatively concentrated sulfuric
acid or hydrochloric acid." This behavior is more nearly what one
would expect if the ferric oxide were adsorbed by the oil than if ferric
salts of fatty acids were formed; but there is no proof either way.[82]

Turning to the fixing of metallic mordants by phosphates, silicates,
etc., we know that in many cases no definite compounds are formed.
In earlier chapters it has been pointed out that hydrous aluminum
oxide adsorbs arsenic acid, hydrous ferric oxide adsorbs arsenious acid
and arsenic acid, hydrous beryllium oxide adsorbs arsenious acid, and
hydrous stannic oxide adsorbs phosphoric acid. In none of these
actions is a definite compound formed, and it is probable that many
more of the alleged phosphates, stannates, and silicates of the heavy
metals are not obtained under ordinary conditions. However, this
does not preclude the formation of definite compounds under special
conditions. For example, crystalline aluminum orthophosphate
results on treating a concentrated solution of sodium aluminate with
an excess of phosphoric acid and heating in a sealed tube at 250° for
several hours.

The nature and properties of color lakes will be taken up in the
next chapter.

[81] "A Manual of Dyeing," 2, 597 (1916).
[82] Cf. Bancroft: J. Phys. Chem., 19, 50 (1915).

CHAPTER XVI

COLOR LAKES OF THE HYDROUS OXIDES

In the dyeing of mordanted cloth, the color is taken up chiefly by the mordant, giving a color lake on the fiber. The most common color lakes are formed with dyes and the hydrous oxides. For a long time such lakes were believed to be definite chemical compounds between the dye and the oxide. This belief was based largely on the observation that acid dyes in which the anion is the colored radical are taken up to a great extent only by basic mordants and basic dyes only by acid mordants. Thus alumina takes up the acid dye alizarin under suitable conditions, and it was assumed that a definite aluminum alizarate was formed. Biltz[1] was the first to suggest that the alizarin lakes might not be definite chemical compounds. He showed, for example, that the amount of alizarin SW taken up by hydrous chromic oxide varies continuously with the concentration of dye and no chromium alizarate is formed. Although certain lakes may be definite Dalton compounds, it seems probable, in the light of recent work, that most lakes are adsorption complexes between the mordant and the dye, the composition of which varies with the conditions of formation.

Some typical observations of Ackerman[2] which show the influence of the concentration of dye on the composition of the color lake are given in Fig. 59a and b for the triphenylmethane dye, acid green, and the azo dye, azo-geranine. The hydrous oxides were precipitated from the respective chlorides with ammonia and washed by decantation. It will be noted that all the curves are of the adsorption type, indicating the absence of compound formation between dye and oxide.

In the experiments summarized in Fig. 59 the concentration of the dyes was the only variable. Since the hydrogen ion concentration is such an important factor in the fixing of dyes on fibers,[3] it would

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[1] Ber., **38**, 4143 (1905).

[2] J. Phys. Chem., **36**, 780 (1932).

[3] Pelet-Jolivet: "Die Theorie des Färbeprozesses" (1910); Bancroft: J. Phys. Chem., **18**, 1, 118, 385 (1914); Briggs and Bull: **26**, 845 (1922).

be expected to influence the taking up of dyes by mordants.[4]   Moreover, observations on adsorption of ions from mixtures of electrolytes would seem to indicate that the concentration of ions present in a dye bath, including hydrogen and hydroxyl, might be quite as important in determining the composition of a color lake as the concentration of the dye itself.   Furthermore the nature, physical character, and purity of the mordant would be expected to influence the compo-
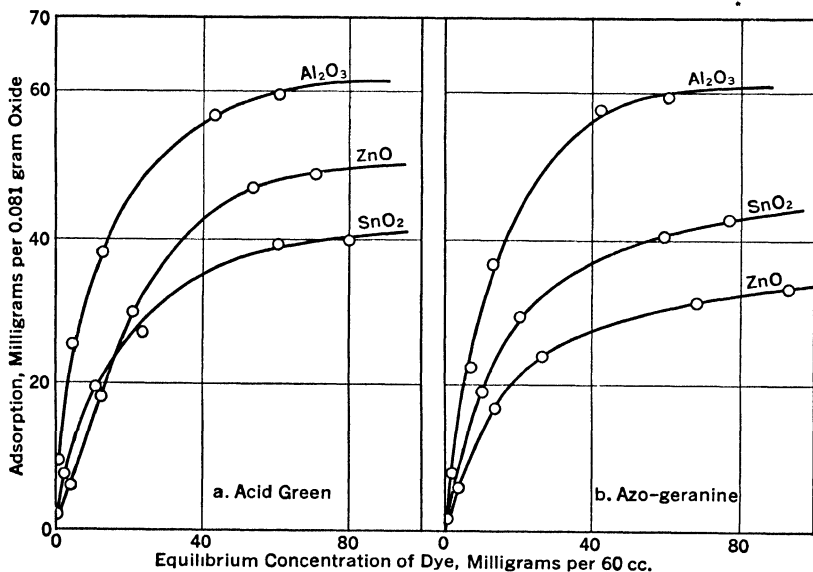
FIG. 59.—Adsorption of dyes by hydrous oxides.

sition of the lake.   The importance of the several factors is strikingly illustrated in the alizarin lakes, which will be considered in some detail.

ALIZARIN LAKES

Alizarin or dihydroxyanthraquinone is the most important mordant dye.   The chief mordants for the dye are alumina which ordinarily yields a red lake, chrome which yields a reddish brown, tin which gives an orange, and iron which gives a purple or black.   In the presence of the so-called sulfonated oils, alumina gives the fast, brilliant red color lake known as Turkey red.

Since hydrous chromic oxide adsorbs alizarin more strongly than

[4] *Cf.* Gordon and Reinmuth: Ind. Eng. Chem., **15**, 818 (1923); Marker and Gordon: **16**, 1186 (1924).

either hydrous ferric oxide or alumina, the most comprehensive series
of experiments were carried out with that mordant.

Adsorption of Alizarin SW

The sodium salt of alizarin monosulfonate was used instead of
alizarin in the initial studies in the author's laboratory[5] for the follow-
ing reasons: it is easy to determine quantitatively even in small
amounts; it is not reduced at the hydrogen electrode in dilute solution;
the acid is sufficiently soluble that no precipitation takes place through-
out a wide pH range; and finally, it is readily purified and weighed.
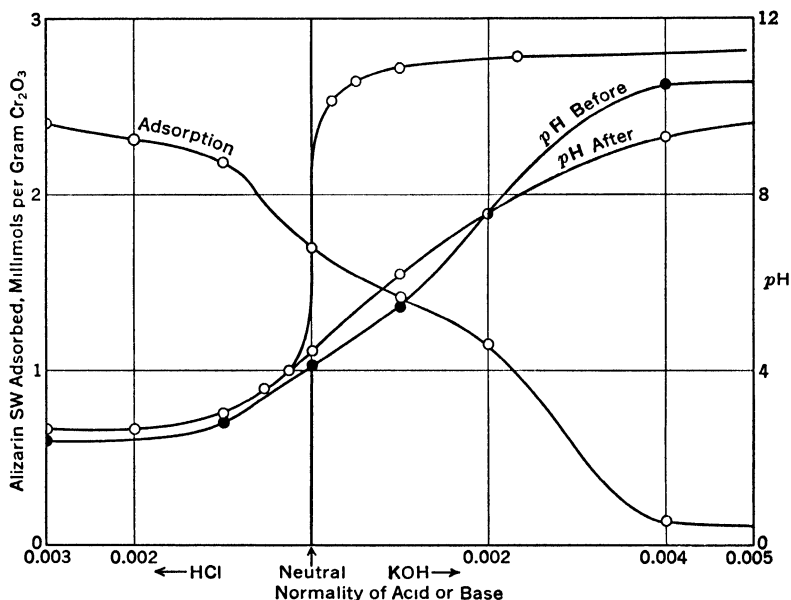
FIG. 60.—Adsorption of alizarin SW by hydrous chromic oxide at varying pH values.

Effect of the pH Value. The adsorption of alizarin SW at varying
pH values was determined by the same general method of procedure
as was used in measuring the adsorption of sulfate (p. 142). The
chromic oxide sol was mixed quantitatively with the dye solution con-
taining varying amounts of acid or base and the adsorption determined
from the change in concentration of dye in the supernatant solution
above the resulting lake. The pH value was found with the hydrogen
electrode in the supernatant liquid (after adsorption) and in a similar
mixture in which distilled water was substituted for the sol (before
adsorption). The data are represented graphically in Fig. 60. For

[5] Weiser and Porter: J. Phys. Chem., **31**, 1824 (1927).

purpose of reference the pH curve for the acid and alkali alone in the same total quantity of water is included in the figure.   The length of a horizontal line drawn from any point on the curve for the pH of the mixture "before adsorption" to the acid-alkali curve gives the quantity of acid or base reacting with the dye at that point.

The adsorption curve is continuous, giving no indication of the formation of a compound at any pH value.   As would be expected, quite a buffer effect is observed in the titration of the monosodium to the disodium salt.   Moreover, there is a corresponding holding up of the adsorption-concentration curve in this region.   This has two causes: the concentration of the hydroxyl ions is not increasing in proportion to the alkali added; and, at the same time, the concentration of the highly adsorbable dye ions is rapidly increasing.   Just as was found with sulfate (p. 142) and with oxalate, hydroxyl ion may completely displace the dye, the latter requiring a slightly higher hydroxyl ion concentration than either sulfate or oxalate.   This indicates that the dye is more strongly adsorbed than either sulfate or oxalate, but is not so strongly adsorbed as hydroxyl.

Simultaneous Adsorption of Alizarate SW and Other Ions

Pelet-Jolivet[6] demonstrated that readily adsorbed anions such as sulfate and phosphate cut down the adsorption of acid dyes (*e.g.*, crystal ponceau), and readily adsorbed cations such as magnesium increase the adsorption of acid dyes.[7]   Davison[8] made some qualitative observations on the effect of sulfate ions and of calcium ions on the adsorption of dyes by fibers as well as by alumina.   Thus he finds that 8 g of Na_2SO_4 in 100 cc. of bath prevents the dyeing of wool by crocein violet.   In lower concentrations, the dye is taken up in increasing amounts as the concentration of the sulfate is decreased.   Alumina precipitated from aluminum acetate was found to adsorb certain acid dyes, including alizarin, more strongly than that from aluminum sulfate.   Calcium acetate was found to increase the adsorption of the acid dye crocein orange but to decrease the adsorption of the acid dye acid green.   There are other inconsistencies such as one might expect in qualitative observations.

The addition of sulfate to acid baths which give up their color too rapidly has long been practiced by the commercial dyer.   The sulfate tends to give a more even dyeing of the fabric by decreasing the adsorp-

[6] "Die Theorie des Färbeprozesses," 94, 98, 119, 148 (1910).

[7] Bancroft: J. Phys. Chem., 18, 11 (1914).

[8] J. Phys. Chem., 17, 737 (1913).

tion and by retarding the rate of adsorption of the dye anion.   Some-
times, however, the presence of a very small amount of sulfate is
objectionable.   At one time, Bancroft[9] believed that the purpose of
adding calcium ion as calcium acetate to an alizarin bath is not to
give a calcium aluminum alizarate or calcium chromium alizarate of
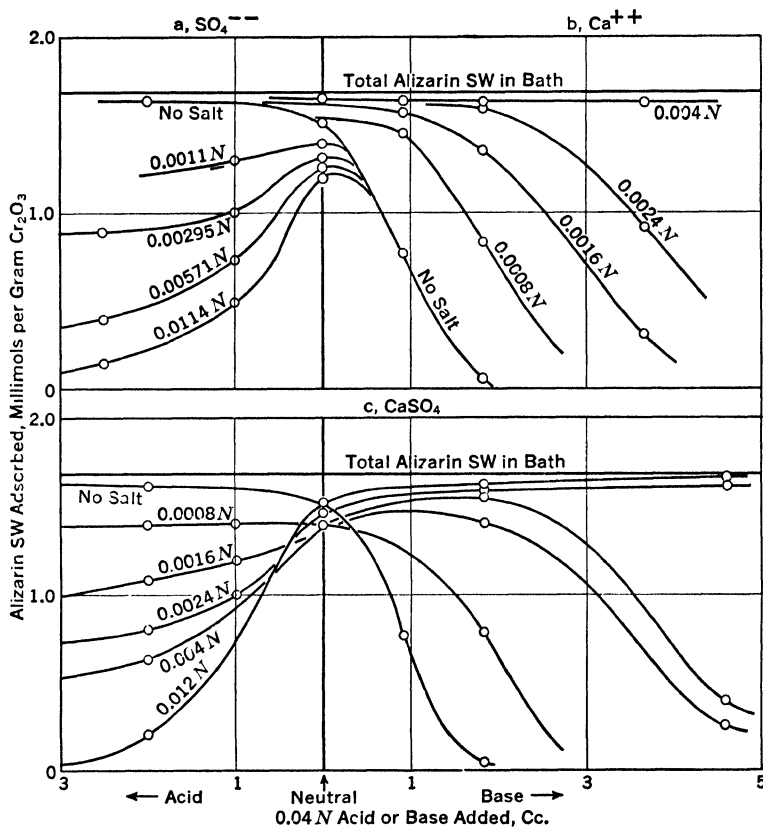
FIG. 61.—Effect of sulfate and calcium ions on the adsorption of alizarin SW by
hydrous chromic oxide at varying pH values.

some sort[10] on the mordanted cloth, but to remove sulfate ion which
cuts down the adsorption of alizarate ion.   As will be seen in the next
section, calcium sulfate is too soluble to enable one to account for the
action of calcium ion in this way.

Effect of Sulfate Ion at Varying pH Values.   The effect of sulfate

[9] J. Phys. Chem., 18, 1 (1914).
[10] Liechti and Suida: J. Soc. Chem. Ind., 5, 525 (1886).

on the adsorption of alizarin SW at varying pH values was determined by essentially the same method of procedure employed in determining the effect of sulfate on the adsorption of oxalate (p. 144). The data are summarized in Fig. 61a. Just as in the case of oxalate, it will be noted that the sulfate has little effect on the adsorption of alizarin SW anion in the neutral and basic solutions since, under these conditions, the presence of the much more strongly adsorbed hydroxyl ion masks the relatively small effect of the sulfate. In the acid range, however, the effect of sulfate is quite marked. Since the dye anion is adsorbed more strongly than sulfate from the same concentration, one might expect the latter to have little effect on the adsorption of the former. But the behavior of the dye is similar to that of the oxalate. In the acid solution the effective concentration of the dye becomes very small because of the suppression of the ionization, and the action of sulfate manifests itself. If the sulfate had been determined in the series of experiments, the results would have been similar throughout to those obtained with sulfate and oxalate, viz., sulfate adsorbed more from the acid bath and dye adsorbed more from the neutral and basic bath. Since acid baths are usually employed in dyeing acid dyes, the retarding effect of sulfate is explained even though the dye cation may be more strongly adsorbed than sulfate ion from the same concentration.

Effect of Calcium Ion at Varying pH Values. The results of the observations on the adsorption of alizarin SW in the presence of varying amounts of calcium ion, as well as varying hydrogen ion concentrations, are given in Fig. 61b. Just as the effect of sulfate ion is small in the presence of the relatively highly adsorbed hydroxyl ion, so the effect of calcium is small in the presence of the relatively strongly adsorbed hydrogen ion.

Effect of Calcium Sulfate at Varying pH Values. Since the foregoing experiments show that the effect of the sulfate is large in the acid and negligible in the basic baths and that the effectiveness of the calcium increases with the hydroxyl ion concentration, one is led to conclude that, if calcium sulfate were present, the effect of the sulfate would predominate in the acid solutions and that the influence of the calcium will be unaffected by the sulfate in the basic baths. Direct experimental verification of this conclusion is given by the data plotted in Fig. 61c. If the curves a, b, and c are superimposed, it will be seen that a and c are alike in the acid range whereas b and c are alike in the basic range. These data show that the effects of the calcium and sulfate ions in the bath are practically independent of each other and that each is dependent on the hydrogen ion concentration.

Adsorption of Alizarin

Effect of Calcium and Sulfate Ions at Varying pH Values.   Sodium alizarate is the dye used in commercial practice.   The results of some observations on the effect of calcium and sulfate ions on the adsorption of alizarin from a sodium alizarate bath are given in Fig. 62.   Since the bath must be basic in order for the dye to remain in solution, one would expect the effect of sulfate to be slight, as the observations show.   On the other hand, the effect of calcium is marked and increases with its concentration.   Hence by the addition of a strongly adsorbed cation one may use a slightly basic bath in which the alizarin is soluble
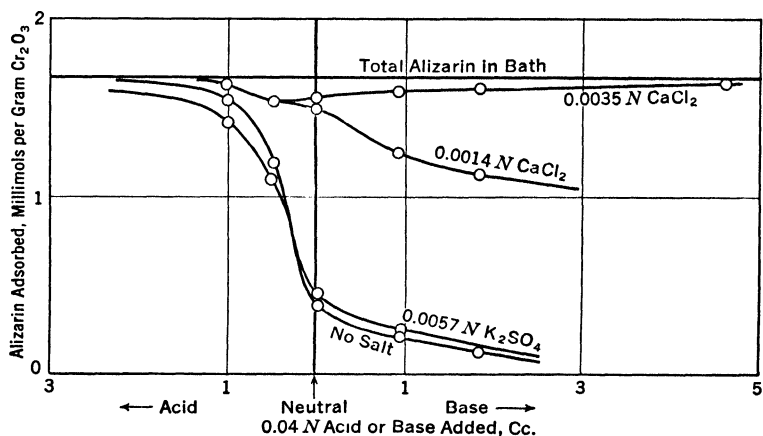
FIG. 62.—Effect of sulfate and calcium ions on the adsorption of alizarin by hydrous chromic oxide at varying pH values.

and at the same time avoid the displacement of the dye anion by the hydroxyl.   This is the function of calcium ion in the formation of alizarin lakes on the fiber.   That the effectiveness of calcium ion is not due to the direct precipitation of alizarin as calcium alizarate is evidenced by the fact that the quantity of calcium present may be greater than the equivalent of alizarin without the dye bath becoming exhausted.   Moreover, the color of calcium alizarate is purple, and since the effect of calcium is to increase the red color by increasing the adsorption of alizarate ion, there is no justification for assuming the formation of purple calcium alizarate on the mordant.

From these considerations the effect on the lake formation process of the addition of salts to the dye bath may be generalized as follows: (1) The presence of a strongly adsorbed cation in the dye bath

increases the rate and quantity of adsorption of acid dyes and has an opposite effect on basic dyes, its effect increasing with the pH of the bath and with its own concentration.   (2) The presence of a strongly adsorbed anion in the dye bath decreases the rate and quantity of adsorption of acid dyes and increases the adsorption of basic dyes, its effectiveness increasing with the acidity of the solution and with its own concentration.   (3) If the dye bath is either acid, or basic the effects of the cations and anions are practically independent of each other, the influence of the cation predominating in the basic bath and of the anion in the acid bath.

Mechanism of the Formation of Alizarin Lakes

Chrome, Alumina, and Iron Lakes.   From the above experiments with chromic oxide and from similar observations with ferric oxide and alumina, it would seem that the alizarin lakes are formed by adsorption of the alizarate ion by the hydrous oxides.   Bull and Adams[11] and Williamson[12] shook a solution of sodium alizarate with the hydrous oxides and concluded that metallic alizarates were not formed since hydroxide equivalent to the alizarate taken up was not set free as would happen if a double decomposition reaction took place.   The absence of an appreciable amount of alkali in the bath led to the further conclusion that the lakes are adsorption complexes between the hydrous oxide and sodium alizarate.   This mechanism appeared unsatisfactory since, as a general rule, positively charged hydrous oxides adsorb the anion rather than the molecule of highly ionized salts.   To settle this point,[5] enough hydrous chromic oxide was added to 100 cc of $N/100$ sodium alizarate to decolorize it, and an aliquot part of the supernatant solution was analyzed for sodium.   It was found that more than 85% of the sodium remained in the bath.   Similar observations were made with ferric oxide and alumina.   Some results with an alumina sol prepared by the action of amalgamated aluminum on water containing a small amount of hydrochloric acid (p. 109) are given in Table XXIII.[13]   As the data indicate, the sodium in the solution after the lake formation is associated with an equivalent amount of chloride displaced from the gel by the more strongly adsorbed alizarate and hydroxyl ion in the original dye bath.   The lake-formation process appears to consist in an exchange adsorption of the dye anion with

[11] J. Phys. Chem., **25**, 660 (1921).

[12] J. Phys. Chem., **28**, 891 (1924).

[13] Weiser: J. Phys. Chem., **33**, 1713 (1929).

TABLE XXIII

ADSORPTION OF ALIZARATE BY ALUMINA

Substances mixed		NaCl in 50 cc weighed as		NaCl		Na₂SO₄	
Sol cc	Sodium alizarate M/100 cc	NaCl	Na₂SO₄	Calculated	Observed	Calculated	Observed
90	25	0.0122	0.0153	0.0293	0.0281	0.0355	0.0352
		NaCl in 75 cc					
80	28	0.0224	0.0291	0.0328	0.0322	0.0398	0.0419

less strongly adsorbed anions on the oxide. Since the sols used in the original experiments were believed to owe their charge to preferential adsorption of hydrogen ion, the resulting lakes were tacitly assumed to be hydrous oxide-alizarin acid adsorption complexes. Bancroft[14] questioned this conclusion on the ground that the alumina-alizarin lake is red and adsorption of the yellow orange alizarin acid would not be expected to give a red lake. As a matter of fact, it is adsorption of the red alizarate ion which gives the red lake since red lakes are formed by mixing a suspension of hydrous, fibrous alumina from amalgamated aluminum and alizarin acid dissolved in alcohol.

Although lake formation usually involves an exchange adsorption, a red alizarin lake results on adding sodium alizarate solution to a freshly prepared gel of alumina from amalgamated aluminum and, hence, free from exchangeable ions. In this case also the red lake results from adsorption of the red alizarate ion rather than of purple, molecular sodium alizarate. A purple lake is obtained when anhydrous alumina adsorbs molecular sodium alizarate from its purple solution in alcohol.[15]

In this connection, it is of interest to note that a hydrous oxide gel free from adsorbed ions ages quite rapidly. Two samples of fibrous alumina were prepared. In preparing the first, special precautions were taken to avoid the presence of chlorine, whereas the second was formed in water containing a small amount of sodium chloride. The adsorption capacity, as indicated by the color of the lake formed with samples of the gel after different time intervals, is given in Table XXIV.[5] It is evident that the chloride-free oxide

[14] J. Phys. Chem., **32**, 955 (1928).
[15] Bancroft and Farnham: J. Phys. Chem., **36**, 3127 (1932).

<div align="center">

TABLE XXIV

ADSORPTION CAPACITY OF Al₂O₃ IN RELATION TO ITS AGE AND CHLORIDE CONTENT
</div>

Age of Al₂O₃	Color of Lake	
	Chloride-free Al₂O₃	Al₂O₃ containing adsorbed chloride
10 minutes............	Dark red	Dark red
16 hours..............	Light red	Bright red
1 day................	Light red	Bright red
2 days...............	Pink	Bright red
7 days...............	Light pink	Bright red

loses its capacity to adsorb dye much more readily than the one containing chloride.

In view of the above observations, one appears justified in concluding that the formation of alizarin lakes of the hydrous oxides under consideration is usually an exchange adsorption process in which the relatively strongly adsorbed dye anion displaces a more weakly adsorbed anion such as chloride from the hydrous oxide. If the adsorption capacity of the gel is satisfied with a strongly adsorbed anion such as hydroxyl, little exchange adsorption can take place and lake formation is prevented. Since a bath must be slightly basic in order for alizarin to remain in solution, the necessary adsorption of alizarate ion for suitable lake formation from such baths takes place only in the presence of a relatively strongly adsorbed cation such as calcium.

Lakes are formed by the addition of sodium alizarate to positive hydrous oxide sols stabilized by preferential adsorption of hydrogen ion. If the accompanying anion is chloride, the amount of alizarate ion taken up by the coagulated oxide is equivalent to the amount of sodium chloride in the supernatant solution. The addition of sodium alizarate above the coagulation value reverses the charge on the sol owing to preferential adsorption of alizarate ion. This was confirmed by Ackerman,[16] who showed further that the negatively charged lake was precipitated by an excess of sodium alizarate. This is a typical example of an "irregular series" (Vol. I, p. 88).

If the gel of alumina, say, is formed rapidly in the absence of an anion such as chloride, highly unsaturated atoms of aluminum on the

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[16] J. Phys. Chem., **36**, 780; cf., also, Bancroft and Farnham: 3127 (1932).

surface will adsorb alizarate ion from aqueous solutions of sodium alizarate or from alcoholic solutions of alizarin, yielding red lakes. On standing, the highly unsaturated atoms on the surface of the newly formed oxide become oriented into the normal lattice of crystalline alumina, and the adsorption of alizarate decreases to such an extent that only a pale pink lake results. The rate and amount of the aging are appreciably diminished by the adsorption of chloride, say, since a part at least of the abnormal unsaturation of surface atoms in the rapidly formed oxide is satisfied by the adsorption. An ion more strongly adsorbed than chloride would have a greater retarding action on the rate at which the atoms assume their position in the normal oxide lattice. But, as we have seen, the presence of an ion more strongly adsorbed than chloride will correspondingly decrease the adsorption of alizarate by exchange.

From these considerations it follows that, depending on the conditions, adsorption of alizarate ion may be either exchange adsorption, direct adsorption, or both. The red color of alumina-alizarin lakes is neither the dark purple to purplish black of the alkali and alkaline earth alizarates nor the orange of the alizarin acid but is a bright red suggestive of the color of the alizarate ion in aqueous solution. The color of the lake is doubtless due to adsorption of the alizarate ion oriented toward the aluminum atom of the oxide. The ion associated with the alizarate ion and oriented toward the oxygen atom of the oxide may be sodium, potassium, ammonium, hydrogen, or calcium without materially modifying the color of the lake except in so far as the extent of its adsorption influences the amount of adsorption of alizarate ion.

The concept that the alumina-alizarin lake consists of alizarate adsorbed on aluminum atoms might be interpreted to mean that the color is due to a definite aluminum alizarate. This appears to be the point of view of Wedekind and Rheinboldt.[17] Such an interpretation would imply that alizarate radicals are bound to aluminum atoms on the surface of the oxide by primary valence forces; in other words, that two aluminum atoms on the surface hold exactly three alizarate radicals. Followed to its logical conclusion this would mean that sodium, ammonium, or hydrogen alizarate adsorbed by aluminum oxide consists of aluminum alizarate plus sodium oxide, ammonium oxide, or water, as the case may be. There is no experimental evidence to justify this conclusion, and it is probably incorrect.

The above observations and conclusions of the author have been

[17] Ber., 52, 1013 (1919).

confirmed in all essential respects by Bancroft and Ackerman[18] and Bancroft and Farnham.[15]

Tin and Zinc Lakes. The hydrous oxides of tin and zinc differ from those of aluminum, chromium, and iron in that the former do not adsorb the red alizarate ion from solutions of alizarin acid or sodium alizarate. For this reason, cherry red alizarin lakes are not obtained with tin and zinc. On the contrary, the latter mordants adsorb molecular alizarin acid (yellow) and sodium alizarate (purple), giving lakes that vary in color from yellow to purple, depending on the pH value of the solution.[19] As we have seen, yellow and purple lakes of alumina are obtained only with anhydrous alumina and solutions of alizarin acid and salt, respectively, in non-ionizing solvents. The so-called yellow alizarin-alumina lakes obtained in the presence of water are mixtures of alizarin acid crystals and alumina.[13] Hydrous tin oxide adsorbs violuric acid (colorless) slightly but no color is produced; hence it is the undissociated acid which is taken up. It does not adsorb violurate ion (purple) nor sodium violurate (red) to give color lakes. On the other hand, alumina adsorbs the violurate ion only, giving purple lakes.[18] It is not obvious why certain hydrous oxides should adsorb chiefly the dye ion whereas others adsorb chiefly the dye molecules.

Dyeing with Alizarin Lake

The commercial process of dyeing Turkey red involves seven more or less distinct operations: (1) bleaching of the fiber, (2) adsorption of some soap-forming oil on the fiber, (3) saponification of the adsorbed oil, (4) removal of the excess soap and oil, (5) mordanting of the soap-containing fiber with alumina, (6) adsorption of calcium and alizarate ions by the mordant, (7) cleaning, which removes the dirt and varnishes the dyed fiber with a very thin film of tin soap.

Since the alumina-alizarin lake is readily peptized by a suitable excess of sodium alizarate (p. 368), Ackerman[20] showed that the procedure for dyeing Turkey red may be simplified by dyeing directly from the lake sol. The fiber adsorbs the mordant which has already taken up the dye. It is possible to vary the color of the lake sol by using different proportions of materials, and different results may be obtained by the use of Turkey red oil before or after the dyeing.

[18] J. Phys. Chem., **35**, 2568 (1931).

[19] Bancroft and Ackerman: J. Phys. Chem., **35**, 2568 (1931); Bancroft and Farnham: **36**, 3127 (1932).

[20] J. Phys. Chem., **36**, 490 (1932).

This procedure for dyeing mordant colors from baths of lake sols would appear to be generally applicable. Ackerman has pointed the way to a new procedure for applying mordant colors which should find wide use in dyeing practice.

CONGO RED LAKES

Congo red, the disodium salt of diphenyl-diazo-bis-naphthalene-4-sulfonic acid, is a red dye substantive to cotton. Aqueous solutions of the dye contain red colloidal ionic micelles (aggregate of simple ions) which are too small and hydrous to be visible in the ultramicroscope but which will not pass a membrane permeable to ions in true solution. Replacing the sodium in Congo red with hydrogen gives a blue colloidal acid. The equation for the reaction may be represented as follows:

$$2Na^+ + R^{--} \text{ (red)} + 2H^+ + 2Cl^- \rightleftarrows H_2R \text{ (blue)} + 2Na^+ + 2Cl^-$$
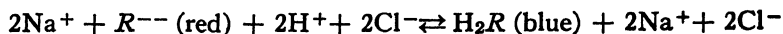
where R stands for the anion of the dye. This blue colloidal acid was shown[21] to be slightly soluble in water, yielding the red anion. The solubility increases with rising temperature. Thus in the blue sol the following equilibria exist:

$$nH_2R \text{ (blue)} \rightleftarrows nH_2R \text{ (in solution)} \rightleftarrows 2nH^+ + nR^{--} \text{ (red)}$$

These conclusions were based on observations in quartz containers since the alkali dissolved from ordinary glass at room temperatures is sufficient to change dilute Congo acid from blue to red.

The hydrous oxides of iron, chromium, and aluminum form stable color lakes with Congo red. From the standpoint of the theory of the lake-formation process, the most interesting Congo red lakes are those obtained by starting with the blue acid. Bayliss[22] found that hydrous alumina adsorbs the blue acid from its colloidal solution; if this adsorption complex is washed, suspended in water, and heated, the color changes from blue to red. Since Congo red salts are red, Bayliss attributed this change in color to the formation of an aluminum salt. The experiments were extended to the precipitates obtained by mixing the blue negative sol with the positive sols of the hydrous oxides of aluminum, zirconium, and thorium. The blue adsorption complex becomes red on heating in every case, provided the hydrous oxide sols are dialyzed until practically free from acid. A small amount of acid is sufficient to prevent the change in color.

[21] Weiser and Radcliffe: J. Phys. Chem., 32, 1875 (1928).
[22] Proc. Roy. Soc. (London) 84B, 81 (1911).

Assuming that the color change is due to the formation of a Congo red salt of aluminum or zirconium, there is no obvious reason why a trace of acid should prevent the change provided there is an excess of hydrous oxide with which the Congo red acid can react.[23]   Blucher and Farnau[24] attempted to get around this difficulty by assuming that the hydrous oxide adsorbs and stabilizes the free red Congo acid, which they erroneously believed to be instable in aqueous solution.

Wedekind and Rheinboldt[17] confirmed Bayliss's observation and suggested, but did not prove, that aqueous sols of the blue acid contain more or less red acid which is changed to a blue isomer by acids. The red lake was believed to be a salt of indefinite composition formed by reaction of alumina with the red acid.

Color of Alumina Lakes

Observations on the color of alumina lakes from Congo red acid prepared under various conditions are summarized in the accompanying tables.[21]   In the first experiments, well-dialyzed sols of dye acid (7 g per l) and of hydrous alumina (1.7 g Al_2O_3 per l) were mixed in varying ratios, and the mixtures in quartz test tubes were placed in water at 100° for 2 hours.   Thereafter, the tubes were allowed to stand 12 hours and the observations noted in Table XXV were made.

TABLE XXV

COLOR OF CONGO RED-ALUMINA LAKES

Sols mixed, total volume 25 cc				Color after heating	
In ccs		In milliequivalents		Precipitate	Liquid
Al_2O_3	Dye	Al_2O_3	Dye		
9	1	0.9	0.0022	Red	Pink
8	2	0.8	0.0043	Red	Pink
7	3	0.7	0.0065	Red	Colorless
6	4	0.6	0.0086	Red	Colorless
5	5	0.5	0.0108	Purple	Red
4	6	0.4	0.0130	Purple	Red
3	7	0.3	0.0151	Purple	Red
2	8	0.2	0.0173	Blue	Red
1	9	0.1	0.0194	Blue	Blue

[23] Bancroft: J. Phys. Chem., 19, 57 (1915).
[24] J. Phys. Chem., 18, 634 (1914).

It will be seen that although a large excess of Al_2O_3 is present at all times, the lakes vary in color from red through purple to blue as the concentration of the dye sol is increased.   It will be noted further that the range of complete mutual precipitation of the oppositely charged sols is narrow.

The effect of acid on the color of a given lake is shown in Table XXVI.   Under the conditions of the experiment, the formation

TABLE XXVI

EFFECT OF ACID ON THE COLOR OF CONGO RED-ALUMINA LAKES

Ingredients mixed in ccs (total volume 25 cc)			Color			
			After 2 days without heating		After heating	
Al_2O	Dye	$N/40$ HCl	Precipitate	Liquid	Precipitate	Liquid
5	2	0.0	Red	Colorless	Red	Colorless
5	2	0.5	Blue	Red	Purple	Colorless
5	2	1.0	Blue	Pale blue	Purple	Colorless
5	2	2.0	Blue	Light blue	Purple	Colorless
5	2	4.0	⎰ No	Blue	Purple	Colorless
5	2	6.0	⎱ Precipitate	Blue	Blue	Colorless

of the pure red lake is prevented by 0.00005 N HCl.   Heating in the presence of acid causes complete coagulation of the sol mixture.

Mechanism of the Lake Formation Process

The mechanism of the formation of Congo red lakes is as follows: As we have seen, the equilibrium set up in the blue sol may be represented by the equation, nH_2R (blue sol) $\rightleftarrows nH_2R \rightleftarrows 2nH^+ + nR^{--}$ (red solution), in which R^{--} represents the red anion of Congo red. Rise in temperature displaces the equilibria to the right.   On mixing the hydrous oxide sol with the blue dye sol, mutual coagulation of oppositely charged particles results in the formation of a blue lake. Following this process, the alumina adsorbs the red colloidal ion, shifting the equilibrium gradually to the right.   The color of the lake ultimately formed depends on the hydrogen ion concentration and the amount of the blue dye.   If the amount of dye is not in excess of the adsorption capacity of alumina for the red anion, the lake will be red.

If there is an excess of the blue dye, the blue color blends with the red, giving purple, or if the excess of blue is sufficiently great the red color is masked completely. Rise in temperature increases the rate at which the adsorption equilibrium is set up. The addition of even a small amount of acid cuts down still further the low solubility of the acid as well as the degree of ionization of the acid, and blue lakes only are formed.

From these considerations it follows that, if the excess of blue dye above the adsorption capacity of alumina for the red anion were such that it would dissolve and become red on heating, the lake should be red when hot and purple to blue when cold. This proved to be true experimentally.

To summarize: the blue lake is the product of mutual adsorption of oppositely charged colloidal particles. The red lake is an adsorption complex between the hydrous oxide and the colloidal Congo red anion. The mechanism of the process is essentially the same with the hydrous oxides of aluminum, chromium, iron, zirconium, and thorium.

ORANGE II LAKES

The typical lakes considered so far appear to be adsorption complexes between the mordant and the dye rather than compounds of definite composition. That a definite chemical compound is sometimes formed under special conditions is well illustrated by the acid dye, orange II, and alumina. Marker and Gordon[25] observed that little dye was taken up by an alumina gel until a pH value of approximately 3 was reached, when the amount carried down increased enormously. The break in the pH-adsorption curve was attributed to the formation of a definite compound in accord with the following mechanism, where X = the dye radical:

$$\underset{\text{Na}X}{\overset{\text{H}}{\rightleftarrows}} \text{H}X \overset{\text{Al}_2\text{O}_3}{\rightleftarrows} \text{Al}X_3$$

Since metanil yellow shows a similar break in the so-called pH-adsorption curve, owing to precipitation of the dye, which is insoluble in acid, Weiser and Porter[26] attributed the break in the orange II-alumina curve to the precipitation of orange II acid, which was assumed to be relatively weak and but slightly soluble. Actually, the

[25] Ind. Eng. Chem., **16**, 1186 (1924); cf., also, White and Gordon: J. Phys. Chem., **32**, 380 (1928).

[26] J. Phys. Chem., **31**, 1704 (1927).

acid is sufficiently soluble and strong[27] to react with alumina to give an aluminum salt of the dye as claimed by Marker and Gordon and confirmed by Bancroft and Farnham.[15] The aluminum salt is sufficiently soluble to give large well-defined crystals. The evidence is against the formation of a similar ferric salt of orange II, but the ferrous salt has been prepared.

Although alumina and orange II will form a definite salt under suitable conditions, this does not mean that an alumina-orange II lake is always a definite aluminum salt. Paquin in the author's laboratory[28] placed amalgamated aluminum in a solution of purified sodium salt of orange II. The freshly formed fibrous alumina took up the dye strongly from the weakly basic solution. Little or no reduction of the dye could be detected in the process. Some observations summarized in Table XXVII show that the lake is an adsorption complex

TABLE XXVII

ADSORPTION OF ORANGE II BY "GROWN" ALUMINA

Original concentration of Orange II Mols $\times$ 10^{-5} per 200 cc	Time of action of Al	Adsorption of dye Mol $\times$ 10^{-5}	Alumina corrected * Mol $\times$ 10^{-5}	Adsorption Mol NaX per Mol Al$_2$O$_3$
6.494	30	5.344	1.793	0.030
12.98	30	8.96	1.566	0.057
19.48	25	11.13	0.960	0.116
25.98	30	14.18	1.054	0.135
32.47	30	16.94	1.059	0.160
38.97	30	21.14	1.157	0.185

* By subtracting calculated amount of Na$_2$SO$_4$ formed by ignition of dye.

and not a definite compound. Moreover, no color was extracted by repeated washings, as would be expected if the slightly soluble aluminum salt of the dye were formed. Bancroft and Farnham[15] confirmed these observations with ordinary precipitated alumina and orange II sodium salt. As with sodium alizarate and precipitated alumina, the colored anions of orange II are adsorbed in exchange for chloride ions.

That it is not safe to assume a lake to be a true compound simply because the constituents in question can form a definite salt under

[27] Sisley: Bull. soc. chim. (3) 25, 862 (1901); Reinmuth and Gordon: Colloid Symposium Annual, 7, 161 (1930).

[28] Weiser: Alexander's "Colloid Chemistry," 4, 507 (1931).

special conditions is further emphasized by the work of Gilbert[29] on the copper lakes of eosin. Gilbert prepared a definite crystalline copper eosinate, but found it to be a different substance from the precipitate obtained by the interaction of copper sulfate and sodium eosinate. Although the precipitated lake has a fairly constant composition, it always contains an excess of copper when an excess of copper salt is employed. By shaking hydrous copper hydroxide with varying concentrations of an ether solution of eosin, a typical adsorption isotherm is obtained, showing no evidence of compound formation. The maximum amount of eosin adsorbed under these conditions is only about one-tenth of that necessary to form copper eosinate. Starting with colloidal copper hydroxide and colloidal eosin acid, lakes were obtained varying in composition between 2 molecules of copper to 1 of eosin and 2 molecules of eosin to 1 of copper. All the lakes behave like the one in which copper and eosin are in equivalent quantities, and all can be carried into colloidal solution. In the presence of ether, small amounts of certain salts decompose the lakes. This is because the adsorption of the anions of the salts by hydrous copper hydroxide is sufficiently great to displace the adsorbed eosin. The order of displacing power of the anions is the usual order of adsorption: $SO_4^{--} > Br^- > Cl^- > NO_3^-$.

Similarly, the taking up of crystal ponceau by wool mordanted with alum was shown by Pelet-Jolivet[30] to be a clear case of adsorption when the process is carried out at room temperature; but at 90°, the amount taken up is practically independent of the concentration of the dye bath so long as it contains more than 700 mg per 1, the lowest concentration employed. It is probable that, in this instance, a definite aluminum salt of crystal ponceau is formed. Pelet-Jolivet prepared such a salt in crystalline form.

METHYLENE BLUE LAKES

Methylene blue is a typical basic dye, the cation being the colored radical. Pelet-Jolivet[31] showed that this dye is adsorbed by the acid mordant silica, the amount taken up varying continuously with the concentration of the solution. He observed also that the extent of adsorption is determined by the age and the previous history of the mordant. Marker and Gordon[32] obtained a smooth curve for the

[29] J. Phys. Chem., **18**, 586 (1914).
[30] "Die Theorie des Färbeprozesses," 213 (1910).
[31] "Die Theorie des Färbeprozesses," 71, 205 (1910).
[32] Ind. Eng. Chem., **16**, 1186 (1914).

amount of dye taken up by hydrous silica at varying pH values; but a sharp break in the pH-adsorption curve was observed with the basic mordants, ferric oxide and alumina, at a pH value near 11. Marker and Gordon imply that the lake formed in all cases is a chemical compound; but until someone shows that a very weak base like methylene blue will react with ferric oxide to give a stable salt under special conditions, there is no apparent reason for assuming that the iron-methylene blue lake as ordinarily formed is ever a definite chemical compound. In Fig. 63 are given the results of some observations on the adsorption of the dye cation by hydrous ferric and chromic oxides at varying pH values.[26] Since we are dealing with a basic dye, it is
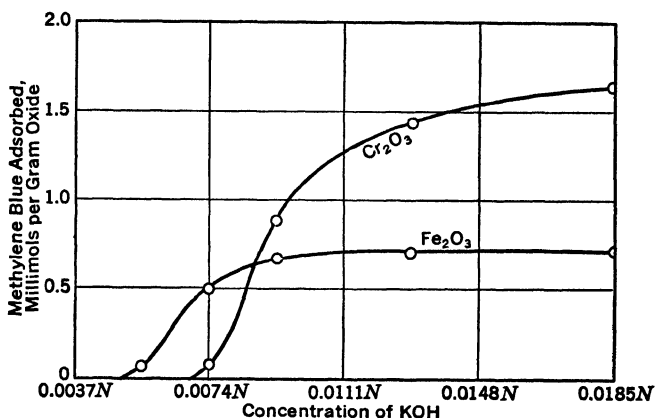
FIG. 63.—Adsorption of methylene blue by hydrous ferric and chromic oxides at varying pH values.

not surprising to find that there is little adsorption by the positive sols. In both cases the adsorption starts sharply at the concentration of alkali which, in the absence of the dye, starts peptization of the hydrous oxides as negative sols. Above the pH values necessary to start lake formation, the amount of methylene blue cation adsorbed is a measure of the negative charge introduced by the adsorption of hydroxyl ion; hence it corresponds to the hydroxyl ion adsorption isotherm. In this connection, it was noted that the maximum adsorption of methylene blue cation is obtained in the presence of the same concentration of hydroxyl ion which, in the absence of the dye, gives complete peptization of the oxide as a negative sol. At still higher pH values, the adsorption of methylene blue falls off. A similar behavior in the adsorption of methylene blue by wool was observed

by Briggs and Bull,[33] who assigned the effect to the increase in the colloidality of the dye in the basic solution. Since the cation of the dye is adsorbed, the suppression of the dissociation of the weak base might also be an important factor.

From the above survey of the mechanism of the formation of some typical color lakes of the hydrous oxides, one seems justified in concluding that the lakes are usually adsorption complexes.[34]   In certain cases definite salts may be formed, but these constitute the exceptions to the general rule.

THE FADING OF COLOR LAKES

Not only does the use of mordants serve to fix certain dyes on fibers, but also the resulting color lakes are in general more stable to light than the dye alone.[35] Lakes prepared from colored mordants, such as iron, chrome, and copper, are more stable to light than those from colorless mordants, such as alumina, zinc, and tin, since the former, acting like color screens, cut off some of the effective rays.   In general, the more strongly a dye is adsorbed by a mordant the slower it will fade on exposure to light. For example, in Fig. 59 we have seen that acid green is adsorbed by different mordants in the order: alumina > tin > zinc; in this case, the alumina lake is most stable to light, the zinc lake least stable, and the tin lake occupies an intermediate position. With azo-geranine the adsorption by the zinc mordant is stronger than by the tin mordant, and the stability of the series of lakes is in the order: alumina > zinc > tin. Aging of a mordant cuts down its adsorption capacity for dyes and thereby decreases the stability of the corresponding lakes toward the action of light. For example, an aged alumina adsorbs acid green less strongly than fresh stannic oxide, and in this case, the alumina lake is less stable than the tin lake.

[33] J. Phys. Chem., 26, 845 (1922).
[34] Cf. Pavelka and Heisnar: Kolloid-Z., 66, 340 (1934).
[35] See Ackerman: J. Phys. Chem., 36, 780 (1932).

CHAPTER XVII

MINERAL TANNING

Tanning is the process whereby the skin or hide of animals is converted into leather. The dermis or leather-producing portion of the skin is made up of bundles of fine connective-tissue fibers about 1μ in diameter, bound together irregularly. The fibrils are composed of a protein material, collagen, which is converted into gelatin by boiling with water. The tanning process consists essentially in coating the fibrils with a film which prevents their adhesion into a hard mass on drying and protects them from the action of water and dilute alkali.

To prepare the skin for tanning it is first soaked in water to rehydrate it and to remove extraneous matter, including salt, in the case of salted skins. It is next immersed in saturated lime water to which is usually added sodium sulfide to "sharpen" or hasten the action of the lime. The liming process not only removes the hair and destroys the epidermis but also swells the collagen fibers and removes a part of the cementing material between them, thereby splitting the bundles into their constituent fibrils. After the removal of the hair, together with certain epidermal material and adipose tissue, heavy skins are often "delimed" by placing in a bath of dilute organic acid. With light skins, the chemical deliming is usually replaced by a process called "bating," which subjects the skin to the action of pancreatic enzymes whereby, among other effects, the remaining interfibrillary substance and reticular tissue are digested.[1] For chrome tanning the bated skin is next "pickled" in a solution of sodium chloride and sulfuric or hydrochloric acid in amount depending on the basicity of the chrome liquor employed. In any case, after all undesirable impurities are removed from the skin and the collagen fibrils are brought to a flaccid, slightly swollen condition, the skin is ready for the tannage proper. In general, if the skin is soaked in aqueous infusions of woods, roots, barks, fruits, or galls which contain members of the class of organic compounds known as tannins, the process is called vegetable

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[1] *Cf.* McLaughlin, Highberger, O'Flaherty, and Moore: J. Am. Leather Chem. Assoc., **24**, 339 (1929).

tanning, and if the tanning liquor is a mineral salt, it is known as mineral tanning. A consideration of vegetable tanning lies without the scope of this book.

CHROME TANNING

Any mineral salt may be employed for tanning leather provided it undergoes hydrolytic dissociation forming a colloidal hydrous oxide or basic salt. Actually, only the salts of iron, aluminum, and chromium have been employed, and of these the salts of chromium are by far the most important.

The Tanning Bath

Formation. As early as 1858, Knapp[2] described a process for tanning hide with solutions of salts of aluminum, iron, and chromium, but the first successful method of mineral tanning was invented by Augustus Schultz in 1884. In Schultz's "two-bath process," the skins are treated with an acidified solution of potassium dichromate until the liquor penetrates them thoroughly, after which they are put into a bath of acidified sodium thiosulfate which reduces the chromate in the hide to chromic salt, the tanning agent. In 1893 Dennis revived and patented Knapp's original "single-bath" tan liquor which consists of a partially neutralized solution of chromic chloride. Dennis prepared the bath by dissolving chromic oxide in hydrochloric acid and subsequently rendered this more basic by adding caustic soda. Later, Procter[3] showed that good tanning liquors can be prepared by reducing bichromate solution with glucose in the presence of enough hydrochloric acid to leave the solution basic. Basic chromic sulfate was found to be superior to the chloride for one-bath tanning and is now almost universally employed.[4] A useful method of preparing a satisfactory bath consists in the reduction of a strong solution of sodium bichromate directly with sulfur dioxide.[5] A concentrated liquor can be obtained in this way and diluted as required. Technical tanning liquors are also formed by adding sodium carbonate and common salt to solutions of chrome alum.

Constitution. The basic chromic sulfate bath so widely used in chrome tanning is probably colloidal in nature. Thus Wintgen and

[2] "Nature and Essential Character of the Tannin Process and of Leather" (1858); English translation, J. Am. Leather Chem. Assoc., **16,** 658 (1921).

[3] Leather Trades' Rev., Jan. 12 (1897).

[4] Wilson: "The Chemistry of Leather Manufacture," Easton, 278 (1923).

[5] Balderston: J. Am. Leather Chem. Assoc., **12,** 655 (1917); Procter: **13,** 582 (1918); **14,** 30 (1919).

Löwenthal[6] ultrafiltered a so-called one-third basic commercial tan liquor prepared by mixing 20 g chrome alum in 170 cc with 7 g sodium carbonate in 20 cc of water. Using a thick, fine, hardened ultrafilter and applying a pressure of 75 atmospheres, they obtained a filtrate consisting of chromic salt in molecular solution and a residue possessing the appearance and properties of hydrous chromic oxide. Indeed, Stiasny[7] points out that the tanning capacity of a bath begins to be of practical value only after the molecules or molecular aggregates are large enough to be classified as semi-colloidal. In opposition to this, Seymour-Jones[8] attempted the ultrafiltration of a tanning bath containing 270 g Cr_2O_3 per l, prepared by reduction of a solution of sodium bichromate with sulfur dioxide. The solution passed unchanged through a collodion disk ultrafilter and through filter papers impregnated with 1 and 5% gelatin solutions, respectively, and subsequently hardened. This was taken to mean that colloidal chromic oxide or basic salt plays no rôle in chrome tanning. The possibility is not excluded, however, that Seymour-Jones could have ultrafiltered some chromic oxide from his tan liquor if he had used a sufficiently dense filter. On the other hand, one can tan leather to a certain extent in a pure chromic salt solution containing little or no colloidal oxide.

It is not known with certainty whether the aggregates in a practical tan liquor are essentially hydrous chromic oxide with adsorbed sulfate, or basic chromic sulfate. Stiasny[9] considers that they are Werner complexes: (1) hydroxo-chromium compounds such as $[Cr(OH)_2(H_2O)_4]_2SO_4$; and (2) ol-compounds such as

$$[(H_2O)_4Cr \underset{\displaystyle \underset{H}{O}}{\overset{\displaystyle \overset{H}{O}}{\diamond}} Cr(H_2O)_4](SO_4)_2$$
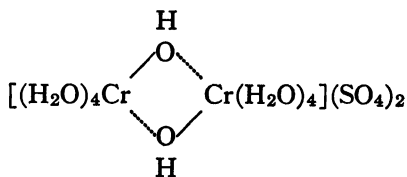
which are formed by the process of olification, that is, the union of two or more chromium nuclei containing hydroxo-groups to give an enlarged nucleus. It is assumed that the complexes are taken up

[6] Kolloid-Z., **34**, 294 (1924).

[7] Alexander's "Colloid Chemistry," **4**, 421 (1932); J. Am. Leather Chem. Assoc. **28**, 383 (1933).

[8] Ind. Eng. Chem., **15**, 75, 265 (1923).

[9] Alexander's "Colloid Chemistry," **4**, 421 (1932); J. Am. Leather Chem. Assoc. **28**, 383 (1933); *see, also*, Gustavson's papers in J. Am. Leather Chem. Assoc., **18–22** (1923–27).

by the hide to give leather. The increasing resistance to hydrolysis by dilute acids and alkali, which leather undergoes on aging, is attributed to further olification in the chromium-collagen compound. He assumes further that the ol-groups give up water and are converted into oxygen bridges or oxo-groups which hold the central chromium atoms together and are more resistant to neutralization than the ol-groups.

Although Stiasny's view of the constitution of basic chromic sulfate baths may be correct, there is no direct experimental evidence to prove it. No one has succeeded in isolating the complex olified chromium sulfate which he assumes to be present in the tan bath, and until this is done, the author prefers the simpler assumption that the aggregates are either hydrous chromic oxide or some simple basic salt, with adsorbed sulfate. In this connection, Wilson[10] writes that: "the ideas here given of olification and aging are highly speculative. At the present stage in the development of the theory of chrome tanning, these ideas are very useful in assisting further progress, but our knowledge of the facts are still too meager to permit theorizing with any degree of certainty."

Mechanism of the Tanning Process

The most plausible theory of chrome tanning is that the hide fibrils adsorb from the tan liquor hydrous chromic oxide (or basic salt) which subsequently ages (p. 128), giving a highly protective coating. This film not only keeps the fibrils separated and thereby prevents their coalescence on drying but also protects them from the action of water and dilute alkali. As Rochelle salt dissolves even an aged hydrous chromic oxide, it is not surprising to learn that a chrome-tanned leather is detanned by soaking in a solution of this salt.[11] The detanned leather can be tanned once more by washing and soaking in fresh chrome liquor.

When the above paragraph was first written ten years ago[12] there was little direct experimental evidence to support it. Davison[13] had determined the amount of chromic oxide taken up by hide powder from various concentrations, up to 1.5 g Cr_2O_3 per l, of a single bath chrome tanning solution. On plotting the Cr_2O_3 taken up against the concentration of the residual solution, a continuous parabolic curve

[10] "The Chemistry of Leather Manufacture," 2nd ed., 2, 681 (1929).
[11] Procter and Wilson: J. Soc. Chem. Ind., 35, 156 (1916).
[12] Weiser: "The Hydrous Oxides," McGraw-Hill Book Co., 325 (1926).
[13] J. Phys. Chem., 21, 190 (1917).

was obtained which indicated that the initial step in the tanning process was absorption of hydrous chromic oxide (or basic salt) by the hide. Although Davison's conclusion appears to be correct, it is not altogether justified by his data since he overlooked the fact that he was dealing with three instead of two phases: (1) the equilibrium concentration of Cr_2O_3, (2) the Cr_2O_3 fixed irreversibly by the hide powder, and (3) the Cr_2O_3 which was unfixed in the hide powder.[14] Recently, McLaughlin, Cameron, and Adams[15] carried out experiments similar to those of Davison, but they analyzed the leather directly for fixed Cr_2O_3 after washing out the reversibly adsorbed material. The results of these experiments are so fundamental to the theory of chrome tanning that they will be considered in some detail.

Tanning with Basic Chrome Sulfate. The effect of the concentration and basicity of tan liquor on the amount of Cr_2O_3 taken up by hide are illustrated by the following typical experiments of McLaughlin, Cameron, and Adams. The tan liquor was glucose-reduced plant liquor of 50% basicity, containing 10.5% Cr_2O_3 by weight. This

TABLE XXVIII

TANNING WITH BASIC CHROME SULFATE LIQUORS

17.5% basic liquor			36.7% basic liquor			46.0% basic liquor		
Grams Cr_2O_3 per 100 g hide substance								
Original liquor	Fixed on hide	Unfixed	Original liquor	Fixed on hide	Unfixed	Original liquor	Fixed on hide	Unfixed
6.36	5.21	1.15	9.30	7.98	1.32	9.30	8.75	0.55
8.45	6.00	2.45	10.36	8.58	1.78	10.33	9.61	0.72
10.58	6.49	4.09	11.39	9.22	2.17	11.35	9.76	1.59
12.67	6.94	5.73	12.41	9.64	2.77	12.37	10.75	1.62
14.81	7.23	7.58	13.44	9.83	3.61	13.35	11.50	1.85
16.90	7.40	9.50	14.50	10.16	4.34	14.47	11.75	2.72
19.04	7.76	11.28	16.55	10.58	5.97	16.51	12.45	4.06
21.12	7.90	13.22	18.65	10.98	7.67	18.56	13.29	5.27
23.28	8.22	15.06	20.70	11.32	9.38	20.66	13.65	7.01
....	....	....	22.80	11.61	11.19	22.70	13.86	9.23
....	....	....	....	....	....	24.76	13.99	10.77

[14] Wilson: J. Am. Leather Chem. Assoc., **12**, 451 (1917); Gustavson and Widen **20**, 406 (1925).

[15] J. Am. Leather Chem. Assoc., **29**, 657 (1934).

liquor was diluted as desired and the basicity lowered by adding sulfuric acid and allowing the mixture to stand 7 days before use.

Twenty-five grams of dehydrated skin in the form of pieces ½-inch square were soaked in 100 cc of water in a quart-jar for 1 hour, after which the chrome liquor was added together with sufficient water to make the total volume of liquor in the system 250 cc. The jars were
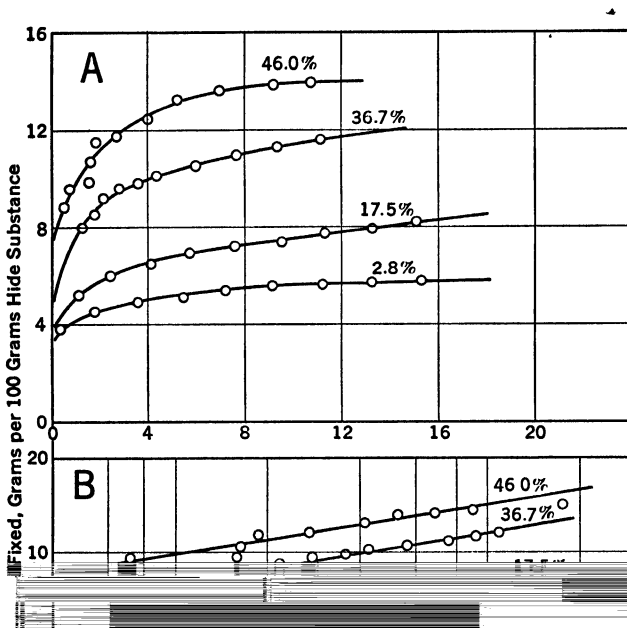
From the parabolic form of the A curves which show the amount of Cr_2O_3 taken up at varying equilibrium concentrations, it would appear that the tanning is essentially an adsorption process involving secondary valence forces rather than a chemical process involving the formation of definite stoichiometric compounds. This is further indicated by the fact that straight lines are obtained (B curves) when the logarithm of the Cr_2O_3 taken up is plotted against the logarithm of the equilibrium concentration of Cr_2O_3. The data emphasize once more the importance of the basicity of the tan bath on the amount of Cr_2O_3 adsorbed: for example, the adsorption from a 36.7% basic liquor is twice as great and from a 46% basic liquor 2.3 times as great as from a 2.8% basic bath.

Observations similar to the above were made on a larger scale using whole calf skins taken from the bate, pickled, and tanned in the tan drums with varying concentrations of glucose-reduced liquors. Three sets of experiments were made with liquors of different degrees of basicity: (1) 31.2%, (2) 35.5%, and (3) 41.6%. In each case, typical adsorption curves were obtained and straight lines resulted when the logarithm of the Cr_2O_3 taken up was plotted against the logarithm of the free Cr_2O_3.

Further laboratory experiments were made with (1) a 24.3% basic chrome alum bath (concentrations 15.3 to 36.8 g Cr_2O_3 per 100 g hide); (2) a 33.2% basic chrome sulfate bath, sodium sulfate free (concentrations 8.16 to 24.5 g Cr_2O_3 per 100 g hide); and (3) a 50.5% basic chrome sulfate bath on pickled hide substance (concentrations 6.3 to 25.2 g Cr_2O_3 per 100 g hide). In all cases the curves were of the typical parabolic type which characterizes adsorption processes.

In similar experiments on the taking up of Cr_2O_3 from a chrome sulfate bath of 36% basicity, Baldwin[16] and Thomas and Kelly[17] obtained curves with a maximum at concentrations of approximately 16 g Cr_2O_3 per l or 67 g Cr_2O_3 per 100 g hide substance. This maximum in the curves was interpreted to mean that a definite chromium collagenate was formed in the tanning process; but the evidence does not warrant this conclusion. Küntzel, Kinzer, and Stiasny[18] have shown that the maximum always results in the presence of sufficient neutral salt which cuts down the amount of Cr_2O_3 adsorbed. The decrease in the amount of oxide taken up in the higher concentrations

[16] J. Am. Leather Chem. Assoc., **14**, 433 (1919).

[17] Ind. Eng. Chem., **13**, 65 (1921); **14**, 621 (1922); *cf.* Gustavson and Widen: J. Am. Leather Chem. Assoc., **20**, 408 (1925).

[18] Collegium, **769**, 213 (1934).

of chrome sulfate liquors is due to the excess sodium sulfate in the baths.

Tanning with Basic Chrome Chloride.   Some tanning experiments with basic chrome chloride similar to those with basic chrome sulfate have been carried out by McLaughlin, Cameron, and Adams.[15]   The results with liquors of different basicities are summarized in Fig. 65. Here, again, typical adsorption curves are obtained (*A* curves), and
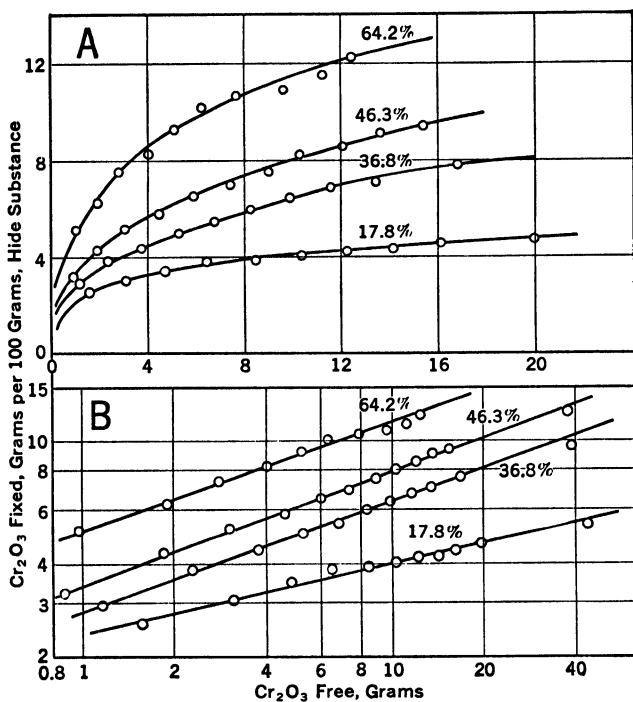
FIG. 65.—Adsorption of Cr_2O_3 by hide substance from chrome chloride tanning liquors of varying degrees of basicity.

when the data are plotted logarithmically, the points lie on straight lines (*B* curves).   For the same degree of basicity of the bath, the adsorption of Cr_2O_3 from the sulfate bath is greater than that from the chloride bath.

Summary.   From the experimental observations recorded above, one seems justified in concluding that chrome tanning is fundamentally an adsorption process, the extent of the adsorption being determined by the basicity, concentration or ratio of Cr_2O_3 to hide substance,

and nature of the liquor employed. The mechanism would appear to be about as follows: If chromic sulfate is placed in solution an equilibrium is set up that may be represented by the equation:

$$Cr_2(SO_4)_3 + xH_2O \rightleftarrows Cr_2O_3 \cdot xH_2O + 3H_2SO_4$$

or, if preferred, by:

$$Cr_2(SO_4)_3 + 12H_2O \rightleftarrows [Cr(OH)_2(H_2O)_4]_2SO_4 + 2H_2SO_4,$$
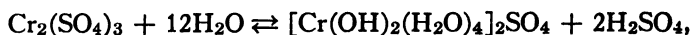
since Werner[19] has prepared a definite crystalline basic salt, insoluble in water, of the formula indicated. When hide is placed in such a solution, it adsorbs both the hydrous oxide and acid shifting the equilibrium to the right; but under these conditions the amount of oxide adsorbed is small at best, and the tannage is relatively light. If, on the other hand, enough of the acid is neutralized or taken up by hide substance to give colloidal oxide (or basic salt), the adsorption of the latter gives a protecting film over the surface of the hide fibrils and the hide is said to be tanned. Obviously, a careful control of the conditions is necessary for successful tanning. In general, if the acidity is too high, the penetration of the liquor into and among the fibrils is good, but the amount of Cr_2O_3 deposited is slight; whereas, if the basicity is too high, the bath contains Cr_2O_3 in too coarse a state of subdivision to penetrate well.

After the tannage is complete, the skin is left in a somewhat acid condition. In practice, it is rendered nearly neutral by treating with a dilute alkaline solution. Even after this treatment chrome leather is characterized by having a relatively high sulfuric acid content. Only a trace is free at any one time, but as soon as this trace is removed, more is immediately liberated. A part of this sulfuric acid is adsorbed by the hide and a part by the hydrous oxide, while some may exist in solid solution in the hydrous oxide or as basic salt.

For a discussion of the purely chemical or stoichiometric theories of chrome tanning, the reader is referred to Wilson's book.[20]

ALUM TANNING

Leather prepared with aluminum salts is less stable than that formed with chromic salts but the former are used in making some kinds of leathers and in the manufacture of some furs. Tanning with aluminum salts is sometimes referred to as "tawing" to distinguish it

[19] Ber., 41, 3447 (1908).
[20] "The Chemistry of Leather Manufacture," 2nd ed., 2, 666 (1929).

from the more vigorous tanning action of basic chrome baths and the vegetable tannins.

An alum tan bath consists of basic aluminum sulfate together with enough sodium chloride to prevent undue swelling of the skin. Since hydrous alumina is not adsorbed very strongly, the freshly treated skin cannot be washed without swelling. Moreover, hydrous alumina ages less rapidly than chrome, and so it is necessary to keep the alum-treated skins in the dried state for weeks or months before a satisfactory leather is obtained. Even at best, alumina-tanned leather is not so permanent as chrome-tanned leather, possibly because hydrous alumina becomes definitely crystalline on aging and so does not afford such good protection to the hide fibrils as does the amorphous film of chrome which never assumes the crystalline form.

IRON TANNING

Basic ferric salts may be employed as tanning agents, but the quality of the resulting leather does not compare sufficiently favorably with that of chrome-tanned leather to justify the use of the cheaper iron salts. According to Procter,[21] a part of the difficulty arises from the fact that ferric oxide acts as an oxygen carrier, causing slow oxidation of the hide and consequent deterioration. Moreover, difficulty is encountered in neutralizing the excess sulfuric acid after tanning. When the leather is treated with a dilute alkali solution, the adsorbed hydrous oxide is displaced, and any normal or basic salt is converted into colloidal hydrous oxide and washed out of the skin.[22] Jackson and Hou[23] claim to have prepared a fairly good leather by adjusting the acidity so as to give a tan liquor in which the ratio of equivalents of hydroxide groups to equivalents of acid radical is never less than 1 : 5 nor more than 1 : 3. After tanning, the neutralization is effected very gradually.

[21] "The Principles of Leather Manufacture," 2nd ed., 275 (1922).
[22] Jettmar: Cuir tech., 8, 74, 106 (1919).
[23] J. Am. Leather Chem. Assoc., 16, 63, 139, 202, 229 (1921).

CHAPTER XVIII

COAGULANTS IN WATER PURIFICATION

Coagulants are the agents added to waters for the purpose of coagulating and removing colloidal material in the process of purifying municipal water supplies.   The objectionable colloidal matter in surface waters consists of finely divided particles of clay, sand, organic coloring matter, and bacteria.   When the contamination is not too great, the turbidity and color as well as the bacteria may be removed satisfactorily from the water by filtration through a slow sand filter without the addition of coagulants.   In this type of filter the filtering sand becomes coated with a slimy protoplasmic deposit called the "schmutzdecke" which consists essentially of myriads of living forms —diatomes, fungi, blue and green algae, protozoa, and bacteria— together with silt, mud, and other colloidal matter.   This protoplasmic layer acts as an ultrafilter which holds back most of the objectionable colloids.   When the water is too turbid or too highly colored, much better results are obtained by the addition of suitable coagulants followed by filtration through mechanical filters.   In this connection, Flinn, Weston, and Bogert[1] say: "For a water having a turbidity[2] less than 30 p.p.m. (parts per million) or a color[3] less than 20 p.p.m., slow sand filters without coagulation give excellent results.   For waters having a turbidity of more than 50 p.p.m. or a color of more than 30 p.p.m., mechanical filters give unquestionably better results. They not only produce an equally safe water but one of far better appearance.   Between these extremes is a region where either the mechanical filter or the slow sand filter with coagulants may be used equally well.   Under ordinary conditions, the latter is far more expensive than the former."

[1] "Waterworks Handbook," 734 (1918).

[2] The standard of turbidity is a water which contains 100 p.p.m. of precipitated fuller's earth in such a state of fineness that a bright platinum wire 1 mm in diameter can just be seen when the center of the wire is 100 mm below the surface of the water and the eye of the observer is 1.2 m above the wire.   The turbidity of this standard water is 100.

[3] The standard color solution, having a color of 500, contains 1.246 g K_2PtCl_6, 1 g $CoCl_2 \cdot 6H_2O$, and 100 cc conc. HCl in 1 l.

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TECHNICAL COAGULANTS

A satisfactory coagulant accomplishes three things: In the first place it neutralizes the charge on the colloidal particles in the water to the point where they coagulate into aggregates which precipitate out. Secondly, under suitable conditions it gives a highly adsorbent hydrous oxide precipitate or floc which adsorbs and entangles most of the finely divided impurities as it settles out. Finally, after most of the floc has settled and the supernatant water has reached the filters, the small residual amount of hydrous oxide forms rapidly, on the filtering sand, a gelatinous filtering layer which retains most of the remaining impurities. When the raw water has a very high bacterial count, it may be necessary to sterilize it with chlorine, hypochlorite, or ozone as an added precaution against transmitting such diseases as typhoid fever and Asiatic cholera. Copper sulfate is frequently added to municipal raw-water supplies to control algae growth. Brockman[4] has shown that this copper sulfate is completely removed by adsorption on either the alum or iron floc provided the pH value is properly adjusted.

Since the colloids in natural waters are negatively charged for the most part, the coagulant should contain a multivalent cation. In technical practice, salts of aluminum and iron are almost always used. Of the coagulants listed in Table XXIX, alum has been employed

TABLE XXIX

TECHNICAL COAGULANTS

Ingredient	Name
$Al_2(SO_4)_3$	Alum
$Al_2(SO_4)_3$ + NaOH (in solution, or as a powder)	Sodium aluminate
Hydrous Al_2O_3 peptized by $FeCl_3$	Ferric aluminate
$FeSO_4$ with $Ca(OH)_2$	Iron and lime
$Fe_2(SO_4)_3$	Ferric sulfate
$Fe_2(SO_4)_3$ + $FeCl_3$ (by chlorinating $FeSO_4$ solution)	Chlorinated copperas
$FeCl_3$ (in solution)	Ferric chloride

most widely, and ferrous sulphate in connection with lime is next in importance. In recent years ferric salts have been made available for this purpose.

[4] Ind. Eng. Chem., **25**, 1402 (1933); **26**, 924 (1934).

FORMATION OF FLOC

Since the hydrous oxide floc plays such an important rôle in the water purification process, it is important to know what constitutes the most satisfactory floc and how the desired product may be obtained. Some waters may contain enough iron to produce a good floc when lime or soda ash is added; others are normally sufficiently alkaline to precipitate hydrous alumina on the addition of aluminum sulfate; still others require the addition of both the metallic sulfate and alkali. If ferrous sulfate is added, lime must always be used to bring about satisfactory precipitation. Thanks to the work of a number of investigators, the principles underlying the floc-formation process are quite well understood. These principles will be developed in the following paragraphs.

Alumina Floc

It is a well-known fact that hydrous aluminum oxide does not separate from a solution of aluminum salt if the solution is either too acid or too alkaline. Moreover, the range of hydrogen ion concentration in which a precipitate separates is determined in large measure by the nature of the anion associated with the aluminum. Thus we have seen that the chloride rather than the sulfate is employed to prepare alumina sol (p. 106), since the agglomerating action of the univalent ion is so much less than that of the divalent ion. In either case, the range of hydrogen ion concentration in which a precipitate forms rapidly from dilute solutions is comparatively narrow, and the range of complete precipitation is still narrower. The ideal conditions should result in the rapid and complete formation of a floc that settles readily. The experiments to be described illustrate the influence of the several factors on floc formation.

Effect of pH Value. In any precipitation process the highest rate of precipitation will result, under otherwise constant conditions, when the highest concentration of separable materials above the equilibrium concentration is attained. In the present instance the degree of supersaturation of water with hydrous aluminum oxide can be varied either by increasing the total amount of aluminum sulfate added at a given final pH value or by varying the pH value with a constant amount of aluminum sulfate. The importance of the hydrogen ion concentration for floc formation was emphasized first by Wolman and Hannan,[5] and the first systematic laboratory experimentation along this line was

[5] Chem. & Met. Eng., **24**, 729 (1921).

done by Hatfield[6] and by Theriault and Clark.[7]   The latter found the optimum pH value to be between pH = 4.9 and pH = 5.4, using 100 to 400 p.p.m. of alum in solutions buffered with phosphates.   The curve relating pH value to flocculation time is U-shaped (*cf*. Fig. 66), with the two branches approximately parallel.   The branches are closer together the more dilute the solutions; hence the region in which a floc appears is quite narrow when the concentration is of the order of 20–30 p.p.m. such as is employed in plant practice.

The time for floc formation in laboratory tests is greatly influenced by stirring and by the size of the vessel employed.   A precipitate which forms within a minute in a large vessel often requires hours to become visible in a small one.   Apparently, this "volume effect" is only the effect of the volume-surface ratio upon circulation, since mechanical agitation decreases the time for the appearance of a floc. Gentle agitation influences only the time of flocculation and not the amount of precipitate or the optimum pH value for maximum rate. Theriault and Clark showed that the "volume effect" is negligible if not less than 2 l of water is used in the experiments.

The method of Theriault and Clark for determining the optimum conditions for floc formation has been refined especially by Bartow and his collaborators.[8]   Their procedure for a series of observations is about as follows: To each of six 3.5-l jars containing 2 l of distilled water is added a solution of aluminum sulfate to give a concentration of 2 grains per gallon (34 p.p.m.).   After thorough mixing, varying amounts of standard alkali are added to give the desired pH value, and the time of addition is recorded.   Each mixture is stirred continuously with a mechanical stirrer consisting of two 3 by 15 cm blades turning at 52 r.p.m.   The time for the formation of a well-defined floc in each vessel is determined by watching for the appearance of a sharp Tyndall cone produced by rays from 100-watt Mazda lamps falling on the mixture through a 0.95-cm aperture.   The total elapsed time is corrected for the time required to add the alkali.   Finally, after the floc settles, the pH value of the supernatant solution is determined colorimetrically, using "isohydric" indicators of approximately the same pH value as that of the solution being tested.[9]

Some observations of the rate of floc formation when the pH value

[6] Ind. Eng. Chem., 14, 1038 (1922).

[7] U. S. Pub. Health Repts., 38, 181 (1923).

[8] Black, Rice, and Bartow: Ind. Eng. Chem., 25, 811 (1933); Peterson and Bartow: 20, 51 (1928).

[9] Acree and Fawcett: Ind. Eng. Chem. (Anal. Ed.) 2, 78 (1930).

is regulated by sodium bicarbonate and by sodium hydroxide are given in Fig. 66. It is apparent that the floc forms most rapidly at a pH of 7.4 with an unbuffered solution of aluminum sulfate in concentrations representing an average filter-plant dosage. The range of fairly rapid coagulation is narrow for such dilute solutions, emphasizing the importance of pH control. In surface waters the optimum pH value may approach 7.4, but it is usually s m a l l e r. For example, Hatfield[10] reported the best results for the hard, moderately turbid water of Lake St. Claire, Michigan, at pH = 6.1–6.3; and Baylis[11] found that a value between pH = 5.7 and 6.6 was the best for the soft slightly turbid Gunpowder river water of Maryland. Similarly, Dallyn and Delaporte[12] found the optimum conditions for coagulation to be pH = 5.5 and 6.5 for soft, colored, and clear Great Lakes water, respectively; and N o l t e and Kramer[13] observed a minimum of residual alum at pH = 6.5 in a St. Louis plant. Although the data are not strictly comparable because of variations in the experimental pro-
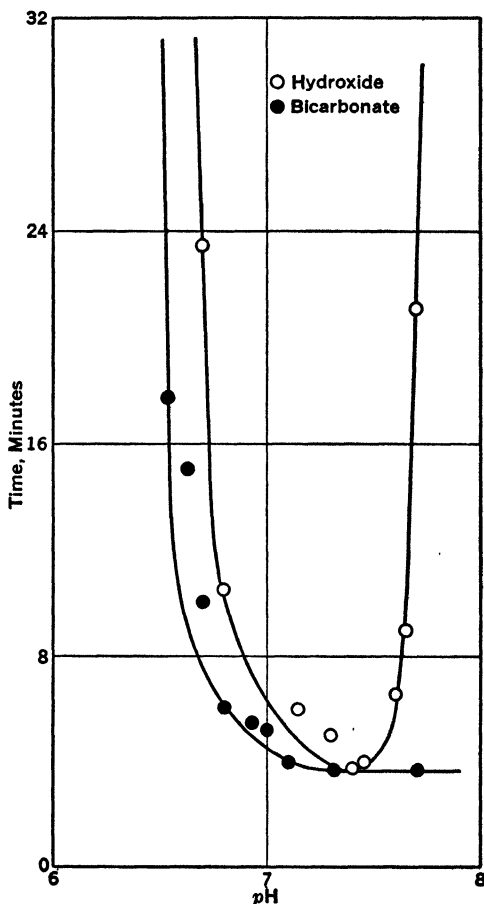
FIG. 66.—Effect of pH value of the solution on the rate of formation of alum floc.

[10] J. Am. Water Works Assoc., 11, 554 (1924).

[11] J. Am. Water Works Assoc., 10, 365 (1923); 15, 22 (1926).

[12] Contract Record, 37, 343 (1923); cf. Catlett: J. Am. Water Works Assoc., 11, 887 (1924).

[13] Ind. Eng. Chem., 25, 1110 (1933); cf., also, Buswell and Edwards: Chem. & Met. Eng., 26, 826 (1922).

cedure, these and a number of other observations that might be cited emphasize the "individuality" in the behavior of surface waters. For this reason each water purification plant must determine the optimum conditions for floc formation with the water with which it is dealing from day to day. This "individuality" is probably due in large measure to the varying salt content of the different waters.

Effect of Sulfate and Other Ions. As already pointed out, the zone of precipitation of hydrous alumina is much wider from aluminum

Legend:
- - - - No SO_4^-
- ○ 25 p.p.m. SO_4^-
- ● 50 p.p.m. SO_4^-
- ◉ 125 p.p.m. SO_4^-

(y-axis: Time, Minutes; x-axis: pH)
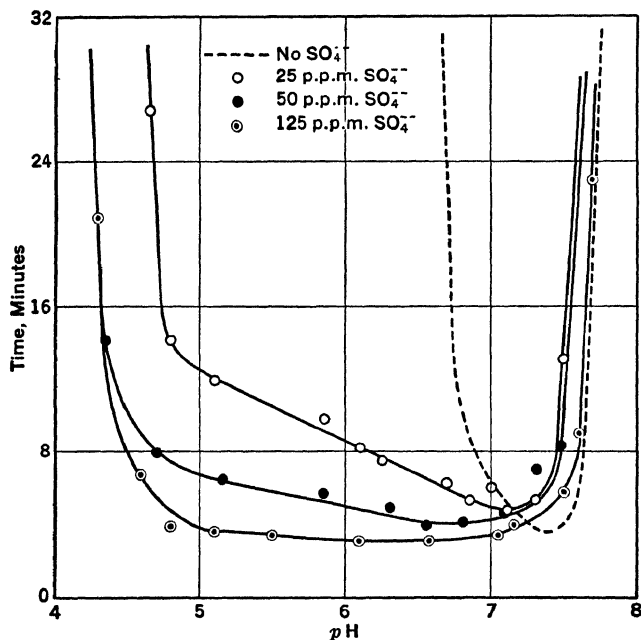
FIG. 67.—Effect of sulfate as Na_2SO_4 on the rate of formation of alum floc at varying pH values.

sulfate than from aluminum chloride.[14] Indeed, it would be altogether impractical to use aluminum chloride alone at the low concentrations employed in plant operation since the oxide remains colloidally dispersed throughout the entire acid range on account of the strong stabilizing action of hydrogen ion and the weak precipitating power of chloride ion. It is obvious, therefore, that the precipitating power of the anions present in solution are equal in importance to that of the pH value in determining the formation of a suitable floc.

[14] *Cf.* Miller: U. S. Pub. Health Repts., **40**, 351 (1925).

From the results of observations with various salts, Miller reports that the sulfate yields a floc best suited to successful water clarification. The range of concentration over which flocculation occurs is relatively broad, and the floc is of good quality, rapid settling, and shows little tendency to become colloidally dispersed.

Since sulfate equivalent to the aluminum has such a marked effect in giving a floc over a limited pH range, it might be expected that the presence in the water of alkali or alkaline earth sulfate would greatly broaden the zone of flocculation. That this is so is demonstrated in a striking way by some observations of Bartow and his collaborators[8] shown graphically in Fig. 67. The pH value was varied by the addition of sodium hydroxide, and varying amounts of sulfate were added in the form of sodium sulfate. The results were obtained by the same procedure and are comparable to those in Fig. 66. Indeed, the dotted curve in Fig. 67 is the same as the curve with NaOH in Fig. 66. It is apparent that the added sulfate broadens greatly the range of rapid floc formation on the acid side, the zone being extended from a pH of about 6.8 to $pH = 4.8$ by adding 125 p.p.m. of sodium sulfate. Calcium sulfate was found to have a similar effect; but sodium chloride in equivalent amounts has little effect in extending the zone of rapid coagulation on the acid side and but slight effect in extending the zone on the alkaline side. The strong precipitating power of sulfate as compared with chloride for positive sols accounts for its much greater effect on the acid side.

If salts such as tartrate or phosphate which have a buffering effect are added to the water, the optimum point is moved well to the acid side, $pH = 5.5–6.0$ instead of 7.4 for the unbuffered solutions. Laboratory tests with buffered solutions give a point not of minimum stability nor of optimum coagulation of the pure floc but of a mixture with different properties. Theriault and Clark's optimum value of 5.5 for the formation of alumina floc, starting with distilled water, was due to the buffering action of the phosphate which they added to the water.

That the laboratory results hold on a semi-plant scale was demonstrated by Black, Rice, and Bartow[15] with the municipal water supply of Gainesville, Florida, having the following mineral content in p.p.m.: SiO_2, 18.7; Ca, 45; Mg, 17; Na and K, 5.2; HCO_3, 179; SO_4, 30; Cl, 10. Some data on this water comparable to those in Fig. 67 are shown in Fig. 68. It will be seen that the optimum pH value for floc formation in the raw water is 7.05 as compared with 7.4 for distilled water, and

[15] Ind. Eng. Chem., **25**, 811 (1933).

that the zone of flocculation on the acid side is wider for the former than for the latter. This is undoubtedly due to the presence of 30 p.p.m. of SO_4^{--} in the raw water. Further addition of sulfate widens greatly the zone of rapid flocculation, as was observed with pure water. In the light of these and similar observations it is now generally recognized that any attempt to establish optimum conditions for floc formation must take into account the effect of salts present in the water,
and especially the anions, of which sulfate is most important in natural waters.
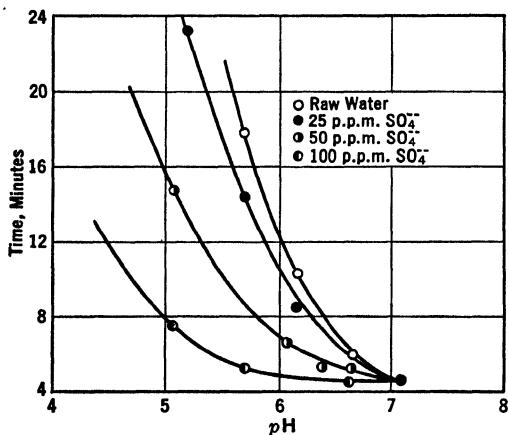
FIG. 68.—Effect of sulfate as Na_2SO_4 in extending the zone of formation of alum floc to the acid side with natural water in an experimental treating plant.

In addition to the negative ion content of surface waters, the presence of colloidal inorganic or organic matter, which may function as protecting colloid, will cause variation in the pH zone where flocculation occurs. Thus colloidal silica[16] prevents the precipitation of hydrous alumina under certain conditions; and sewage-polluted water requires more coagulant than an unpolluted water having the same turbidity and color. From these considerations it may be said that successful water purification by alum depends on the presence of a certain minimum quantity of aluminum ion, the presence of an anion of high precipitating power such as sulfate, and the proper adjustment of the pH value.[17]

The Iron Floc

The so-called iron floc is hydrous ferric oxide. Since the iron oxide is more insoluble than alumina both at higher and lower pH values, the possible pH range of floc formation with the former is broader than with the latter on both sides of the neutral point.[18]

Ferrous sulfate with lime is the most common iron coagulant. It

[16] Smith: J. Am. Chem. Soc., **42**, 460 (1920).

[17] Miller: U. S. Pub. Health Repts., **40**, 365 (1925).

[18] *Cf.* Miller: U. S. Pub. Health Repts., **40**, 1413 (1925).

has been found especially good for turbid, alkaline waters such as those of the Missouri and Ohio Basins. On adding ferrous sulfate to such waters, it acts with the bicarbonate present in the following way:

$$FeSO_4 + Ca(HCO_3)_2 \rightarrow Fe(HCO_3)_2 + CaSO_4$$
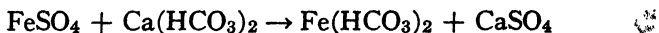
The ferrous bicarbonate oxidizes and precipitates ferric oxide too slowly for practical purposes, so lime must be added, throwing down ferrous hydroxide, thus:

$$Fe(HCO_3)_2 + Ca(OH)_2 \rightarrow Fe(OH)_2 + Ca(HCO_3)_2$$
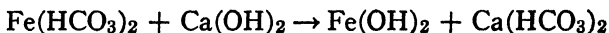
The resulting hydroxide oxidizes very rapidly to hydrous ferric oxide, which constitutes the floc:

$$4Fe(OH)_2 + O_2 + xH_2O \rightarrow 2Fe_2O_3 \cdot xH_2O$$

The ferric oxide floc may be obtained directly from ferric sulfate, ferric chloride, or chlorinated copperas, but until recent years these were not available at sufficiently low cost.

Effect of pH Value (with $FeSO_4$). From investigations to determine the economical pH value for the control of floc formation with ferrous sulfate and lime, Hopkins[19] found, by using 17 to 85 p.p.m. of ferrous sulfate and the requisite amount of lime, that the maximum turbidity removal is at about $pH = 9.4$, which is also the value for maximum precipitation of the ferric oxide floc. In practical operation, satisfactory results are obtained at pH values between 8.8 and 9.2 for a moderately soft water and slightly lower values for harder water. Buswell[20] reports C. A. Brown's recommendation that sufficient lime be added to neutralize the free carbon dioxide, the ferrous sulfate, and enough of the bicarbonate so that the treated water contains not over 6 p.p.m. of normal carbonate. It is obviously necessary to avoid caustic alkalinity.

Effect of pH Value [with $Fe_2(SO_4)_3$]. Some observations of the optimum conditions for floc formation with the ferric coagulants, ferric sulfate and chlorinated copperas, have been made by Bartow, Black, and Sansbury.[21] Following the same procedure as was employed in studying the alumina floc, and working with 27 p.p.m. $Fe_2(SO_4)_3 \cdot 9H_2O$ corresponding to the 34 p.p.m. $Al_2(SO_4)_3 \cdot 18H_2O$ used in the alum experiments, the pH zone in which a ferric oxide floc forms was found

[19] Ind. Eng. Chem., **21**, 58 (1929); "Water Purification Control," 19 (1932).

[20] "Chemistry of Water and Sewage Treatment," 177 (1928).

[21] Ind. Eng. Chem., **25**, 898 (1933); Trans. Am. Soc. Civil Engrs., **98**, 1529 (1933) *cf.*, *also*, Hopkins and Whitmore: Ind. Eng. Chem., **22**, 79 (1930).

to be relatively narrqw, $pH = 5.0-7.0$, and the optimum rate was at $pH = 6.1-6.4$. This is shown in the curve labeled "No SO_4^{--}" in Fig. 69. Similar results were obtained with the chlorinated copperas.

Effect of Sulfate and Chloride Ions [with Fe₂(SO₄)₃]. The effect of added sulfate on the formation of ferric oxide floc, using the same
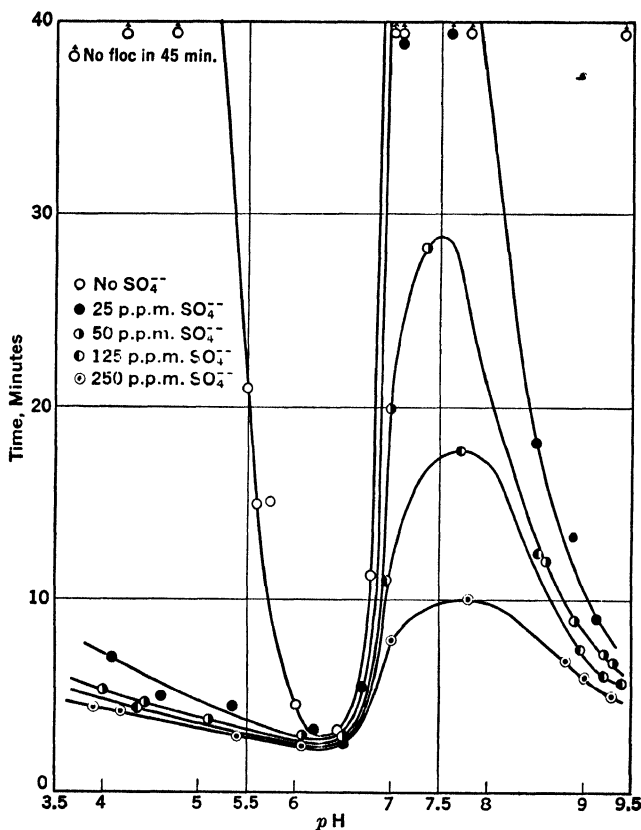
FIG. 69.—Effect of sulfate as Na₂SO₄ on the zone of floc formation with Fe₂(SO₄)₃ at varying pH values.

technique as employed in the preceding experiment, is shown in Fig. 69. It is important to note that the zone of floc formation was greatly widened on the acid side, a floc forming in 4.5 minutes at $pH = 3.9$ with a dose of 25 p.p.m. of sulfate ion. The effect of this small dose on the acid side was almost as great as a dose 10 times as large, in contrast to the behavior of alumina floc, Fig. 67. On the

other hand, the rate of formation of floc was decreased between $pH = 7.0$ and $pH = 8.5$ and again increased at higher pH values. Indeed, a solution containing 25 p.p.m. of sulfate ion, which flocculates rapidly at all pH values between 4.0 and 7.0, does not flocculate in 45 minutes between 7.0 and 8.0. As suggested by Bartow, Black, and Stansbury, this is probably due to a charge reversal of hydrous ferric oxide from positive to negative as $pH = 7.0$ is approached; and adsorption of the added sulfate tends to stabilize rather than to coagulate the sol in the range between $pH = 7.0$ and 8.5. Above this, the coagulating action of sodium ions for the negative sol predominates, and more rapid flocculation again takes place.

As would be expected, chloride ion is not nearly as effective on the acid side as sulfate ion in giving rapid floc formation. On the other hand, the same number of parts per million of sodium chloride is more effective in increasing the rate of the floc formation in the pH range 7.0 to 8.5 than is sodium sulfate. The reason is twofold: the stabilizing effect of sulfate on the negative sol is greater than that of chloride, and the concentration of the precipitating sodium ion is higher in sodium chloride than in sodium sulfate of equal weight. Substituting calcium chloride for sodium chloride gives much more rapid flocculation at pH values above 6.5. In this range, 5 p.p.m. of calcium chloride, which gives the divalent calcium ion, causes more rapid floc formation than 50 p.p.m. of sodium chloride.

Observations similar to the above were made with chlorinated copperas as coagulant.

The Color Floc

The color in water originating in swamps or peaty soils was found by Saville[22] to consist for the most part of negatively charged colloidal particles. Miller[23] confirmed this conclusion and demonstrated further that the decolorizing action on the so-called humic acid colors is due largely to the agglomerating action of the cation of the coagulant, the gelatinous floc playing an unimportant rôle in the process. The precipitating action of hydrogen ion on the negatively charged impurities is much less than that of aluminum ion of the same concentration.[24]

Until the introduction of ferric coagulants, colored waters were always treated with alum. In view of the importance of the alumi-

[22] J. New England Water Works Assoc., **31**, 78 (1917).
[23] U. S. Pub. Health Repts., **40**, 1472 (1925).
[24] *Cf.* Banerji: Indian J. Med. Research, **11**, 695 (1924).

num ion in the coagulation and removal of the coloring matter, it would appear advantageous to treat highly colored waters at a relatively low pH value where aluminum ion exists in solution as such, and after the separation of the color floc, to increase the pH value in order to precipitate all the aluminum. This split treatment is carried out by Norcom[25] with the highly colored Cape Fear River water at Wilmington, N. C. The color floc is precipitated with alum at pH $= 4.4$ and filtered off, after which the residual aluminum oxide is thrown down at pH $= 5.5$ to 6.6. In any event, it is necessary to work well on the acid side,[26] say below pH $= 5.5$, to obtain the color floc, since the negatively charged particles are stabilized in the alkaline range.

Ferrous sulfate with lime is not nearly so good for removing color as alum. This is probably due to the relatively low precipitating power of ferrous ion as compared with aluminum ion and the rapidity with which the former is removed from solution as ordinarily used with lime.

Ferric coagulants should be as good or better than alum coagulants in removing color. Such is true at least in some cases. For example, Hedgepeth, Olsen, and Olsen,[27] using highly colored Elizabeth City, N. C., water, reported excellent results with chlorinated copperas using a split treatment. The color floc was first obtained at pH $= 4.2$–4.7, after which an alkaline coagulant was added, such as sodium aluminate or a mixture of alum and alkali or chlorinated copperas and alkali added simultaneously. Similar results were obtained by Hopkins[28] with the same water using a split treatment of chlorinated copperas (at any pH above 3.5) and lime.

Hedgepeth, Olsen, and Olsen[27] claim that the gelatinous iron color floc has higher adsorptive properties than a true ferric oxide floc.

COMPOSITION OF FLOC

The Alum Floc

Miller[29] determined the composition of the precipitate formed at various final pH values on adding liter quantities of a 0.005 M solution of potassium alum to varying quantities of sodium hydroxide. The

[25] J. Am. Water Works Assoc., 11, 96 (1924).

[26] *For example, see* Yaxley: Eng. News Record, 100, 240 (1928); Enslow: Water Works and Sewage, 76, 227 (1929).

[27] J. Am. Water Works Assoc., 20, 467 (1928); *cf., also,* Decker and Mencke: Water Works and Sewage, 76, 246 (1929).

[28] Ind. Eng. Chem., 21, 58 (1929); Hopkins and Whitmore: 22, 79 (1930).

[29] U. S. Pub. Health Repts., 38, 1995 (1923).

pH values of the resulting solutions were determined and the precipitates were analyzed for their aluminum and sulfate content after thorough washing. The results are given in Fig. 70. Similar results were obtained by Hopkins[30] with dilute solutions such as are used in water-purification processes. From the lowest pH value at which a precipitate forms up to pH = 5.5, the composition of the precipitate remains constant and may be represented approximately by the formula $5Al_2O_3 \cdot 3SO_3$.[31] Above pH = 5.5, which corresponds to 2.4 equivalents of alkali to 1 of aluminum, the sulfate content of the precipitate decreases gradually, becoming zero

FIG. 70.—Composition of alum floc at varying pH values.

at pH = 9.0 when exactly 3 equivalents of alkali to 1 of aluminum have been added.

The constancy of composition of the precipitate thrown down below pH = 5.5 suggests that it may be a basic salt. This view is rendered improbable by the ease with which the sulfate is displaced by washing the hydrous oxide containing sulfate, with solutions of negative ions of equal or greater valence.[32] Dyes containing two or more acid groups, such as the di-, tri-, and tetrapotassium sulfonates of indigo, likewise displace sulfate. From a study of the reciprocal displacement of oxalate and sulfate ions, Miller[33] suggests that the negative ions are in solid solution in the hydrous oxide. This question was considered in an earlier chapter (p. 144), and the conclusion was reached that the carrying down of ions by hydrous alumina is an adsorption phenomenon rather than a case of solid solution in which the ions form an integral part of the space lattice of the microcrystals. A possible explanation of the constancy of adsorption of sulfate ion below pH = 5.5 is that the adsorption of hydrogen ion by the hydrous

[30] J. Am. Water Works Assoc., **12**, 405 (1924).
[31] Williamson: J. Phys. Chem., **27**, 284 (1923).
[32] Charriou: Compt. rend., **176**, 679, 1890 (1923).
[33] U. S. Pub. Health Repts., **39**, 1502 (1924).

oxide reaches the saturation value at approximately this point. If such be the case, the amount of sulfate ion which must be adsorbed to neutralize the adsorbed hydrogen ion will be constant below $pH = 5.5$. Above this value, the adsorption of hydrogen ion falls off, and there is a corresponding gradual decrease in the adsorption of sulfate until it becomes zero at $pH = 9.0$ and above.

The Iron Floc

Hopkins[34] studied the composition of the floc from ferrous sulfate and lime at varying pH values. At normal operating concentrations of ferrous sulfate, the floc appears to be hydrous ferric oxide with little or no adsorbed sulfate. With high concentrations, 428 and 1710 p.p.m., the floc consists of hydrous ferric oxide with adsorbed sulfate, the amount of adsorption decreasing with increasing pH value and becoming zero at $pH = 9.4$, the point of maximum precipitation. The absence of a region of constant composition indicates that no basic salt is formed.[35]

In contrast to the above conclusions, Hopkins claims that a basic ferric salt which he formulates $Fe_2O_3 \cdot SO_3$ is obtained when the floc is thrown down from a chlorinated copperas solution with less than 3 equivalents of alkali to 1 of ferric iron. Although this may be true, the existing evidence is altogether inadequate to establish with certainty that the floc formed at lower pH values, from a ferric coagulant, is a basic salt. It is generally agreed that, when 3 or more equivalents of alkali to 1 of iron are used, hydrous ferric oxide is precipitated

The Color Floc

When the negatively charged colloidal coloring matter is coagulated by adsorption of aluminum or ferric ion, it would be expected that a coagulum of variable composition would result. Hopkins[36] states that the aluminum color floc analyzes for a definite compound of the organic material, and he gives[37] the following formula for the iron floc formed with chlorinated copperas: $Fe_2O_3 \cdot 3H_2O \cdot 2SiO_2 \cdot 4x$, x being the organic constituent. Since it takes more than an analysis to establish for certain whether a colloidal coagulum is a definite compound, the author prefers for the present to regard the color floc as an adsorption complex rather than a definite salt.

[34] Ind. Eng. Chem., 21, 58 (1929).
[35] Cf. Buswell: "Chemistry of Water and Sewage Treatment," 164, 176 (1928).
[36] "Water Purification Control," 14 (1932).
[37] Hopkins and Whitmore: Ind. Eng. Chem., 22, 79 (1930).

APPLICATION OF COAGULANTS

Alum Coagulants

Aluminum Sulfate. Alum is the most widely used coagulant although it is somewhat more expensive than ferrous sulfate. By proper control of the pH value, it can be employed to remove both color and turbidity, but the range of pH value over which it is useful is less than that of ferric coagulants. The alum floc is less dense than the iron floc, and it settles less rapidly.

Sodium Aluminate. In sodium aluminate the alumina is held in strongly alkaline solution and the floc precipitates at once on dilution. This coagulant alone or with alum is characterized by giving more rapid and larger floc formation as compared with alum. Evans[38] lists the following advantages of the coagulant: (1) increased plant capacity due to more rapid settling; (2) less causticity, giving less foaming in boilers; (3) avoidance of increased alkaline sulfates which result from alum or copperas dosage; (4) elimination or material reduction of after-precipitation. Similar advantages have been reported by Ripple, Turre, and Christman[39] in treating the Denver water supply and by Morse, Hechmer, and Powell[40] at Hyattsville, Md. One would not expect the aluminate alone to be useful with water containing large amounts of negatively charged colloidal clay and coloring matter, since it contains none of the coagulating aluminum ion. Treatment with alum to neutralize the colloidal particles, followed by sodium aluminate to give a rapid-settling floc, should yield good results. Sodium aluminate is relatively expensive and will not justify its cost with certain waters.

Colloidal Alumina. Coxe[41] first suggested a coagulant of colloidal alumina formed by adding an insufficient amount of alkali to alum to cause coagulation; and Moberg and Partridge[42] peptized alumina with ferric chloride. Although the positive sol called "ferric aluminate" has not been used technically, it is said to give good results over a smaller and narrow concentration range than is required with alum.

Iron Coagulants

Iron and Lime. As already mentioned, ferrous sulfate is a better coagulant than alum with highly turbid alkaline waters. It is cheaper

[38] U. S. Pub. Health Repts., **43**, 2291 (1928).
[39] Ind. Eng. Chem., **20**, 748 (1928); *cf*. Christman: J. Am. Water Works Assoc., **19**, 629 (1928).
[40] Ind. Eng. Chem., **20**, 56 (1928).
[41] Chem. & Met. Eng., **29**, 279 (1923); *cf*. Spencer: Chem. Age., **32**, 31 (1924).
[42] Ind. Eng. Chem., **22**, 163 (1930).

than alum; it gives a denser, more rapid-settling floc; and the floc does not dissolve at higher pH values as does alumina. Ferrous sulfate must be used with lime and is therefore unsuited for soft waters since any surplus lime would impart a caustic alkalinity. On the other hand, for hard waters the necessary combined use of lime is advantageous since softening occurs as an adjunct to clarification. The ferrous sulfate-lime mixture is not so good for removing color as alum or ferric coagulants because of the low coagulating action of ferrous ion as compared to the trivalent ions.

Ferric Coagulants. Although ferric coagulants have only recently been made available at sufficiently low cost to compete with alum, they are said to have the following advantages over alum:[43] (1) ferric coagulants are useful over a wider pH range; (2) the iron floc is denser and settles more rapidly than the alumina floc; (3) the iron floc does not coat the sand grains of the filter as does the alumina floc.

From the above considerations, it is apparent that the best coagulant to employ in a given case depends both on the nature of the water being treated and on the cost and availability of the treating agent.

[43] Potter and Klein: Water Works and Sewage, **77**, 261 (1930).

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